United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/4-91/001 February 1991

EPA

Ground-Water Issue

SOIL SAMPLING AND ANALYSIS FOR VOLATILE ORGANIC COMPOUNDS

T. E. Lewis, A. B. Crockett, R. L. Siegrist, and K. Zarrabi

The Regional Superfund Ground Water Forum is a group of ground-water scientists that represents EPA's Regional Superfund Offices. The forum was organized to exchange up-to-date information related to ground-water remediation at Superfund sites. Sampling of soils for volatile organic compounds (VOCs) is an issue identified by the Ground Water Forum as a concern of Superfund decision makers.

A group of scientists actively engaged in method development research on soil sampling and analysis for VOCs gathered at the Environmental Monitoring Systems Laboratory in Las Vegas to examine this issue. Members of the committee were R. E. Cameron (LESC), A. B. Crockett (EG&G), C. L. Gerlach (LESC), T. E. Lewis (LESC), M. P. Maskarinec (ORNL), B. J. Mason (ERC), C. L. Mayer (LESC), C. Ramsey (NEIC), S. R. Schroedl (LESC), R. L. Siegrist (ORNL), C. G. Urchin (Rutgers University), L. G. Wilson (University of Arizona), and K. Zarrabi (ERC). This paper was prepared by The Committee for EMSL-LV's Monitoring and Site Characterization Technical Support Center, under the direction of T. E. Lewis, with the support of the Superfund Technical Support Project. For further information contact Ken Brown, Center Director at EMSL-LV, FTS 545-2270, or T. E. Lewis at (702) 734-3400.

PURPOSE AND SCOPE

Concerns over data quality have raised many questions related to sampling soils for VOCs. This paper was prepared in response to some of these questions and concerns expressed by Remedial Project Managers (RPMs) and On-Scene Coordinators (OSCs). The following questions are frequently asked:

1. Is there a specific device suggested for sampling soils for VOCs?
2. Are there significant losses of VOCs when transferring a soil sample from a sampling device (e.g., split spoon) into the sample container?
3. What is the best method for getting the sample from the split spoon (or other device) into the sample container?
4. Are there smaller devices such as subcore samplers available for collecting aliquots from the larger core and efficiently transferring the sample into the sample container?
5. Are certain containers better than others for shipping and storing soil samples for VOC analysis?
6. Are there any reliable preservation procedures for reducing VOC losses from soil samples and for extending holding times?

This paper is intended to familiarize RPMs, OSCs, and field personnel with the current state of the science and the current thinking concerning sampling soils for VOC analysis. Guidance is provided for selecting the most effective sampling device for collecting

Technology Support Project — Communication · Training · Technology Support

Superfund Technology Support Center for Monitoring and Site Characterization

Environmental Monitoring Systems Laboratory Las Vegas, NV

Technology Innovation Office
Office of Solid Waste and Emergency Response,
U.S. EPA, Washington, D.C.

Walter W. Kovalick, Jr., Ph.D., Director

samples from soil matrices. The techniques for sample collection, sample handling, containerizing, shipment, and storage described in this paper reduce VOC losses and generally provide more representative samples for volatile organic analyses (VOA) than techniques in current use. For a discussion on the proper use of sampling equipment the reader should refer to other sources (Acker, 1974; U.S. EPA, 1983; U.S. EPA, 1986a).

Soil, as referred to in this report, encompasses the mass (surface and subsurface) of unconsolidated mantle of weathered rock and loose material lying above solid rock. Further, a distinction must be made as to what fraction of the unconsolidated material is soil and what fraction is not. The soil component here is defined as all mineral and naturally occurring organic material that is 2 mm or less in size. This is the size normally used to differentiate between soils (consisting of sands, silts, and clays) and gravels.

Although numerous sampling situations may be encountered, this paper focuses on three broad categories of sites that might be sampled for VOCs:

1. Open test pit or trench
2. Surface soils (< 5 ft in depth)
3. Subsurface soils (> 5 ft in depth)

INTRODUCTION

VOCs are the class of compounds most commonly encountered at Superfund and other hazardous waste sites (McCoy, 1985; Plumb and Pitchford, 1985; Plumb, 1987; Arneth et al., 1988). Table 1 ranks the compounds most commonly encountered at Superfund sites. Many VOCs are considered hazardous because they are mutagenic, carcinogenic, or teratogenic, and they are commonly the controlling contaminants in site restoration projects. Decisions regarding the extent of contamination and the degree of cleanup have far-reaching effects; therefore, it is essential that they be based on accurate measurements of the VOC concentrations present. VOCs, however, present sampling, sample handling, and analytical difficulties, especially when encountered in soils and other solid matrices.

Methods used for sampling soils for volatile organic analysis (VOA) vary widely within and between EPA Regions, and the recovery of VOCs from soils has been highly variable. The source of variation in analyte recovery may be associated with any single step in the process or all steps, including sample collection, transfer from the sampling device to the sample container, sample shipment, sample preparation for analysis, and sample analysis. The strength of the sampling chain is only as strong as its weakest link; soil sampling and transfer to the container are often the weakest links.

Sample collection and handling activities have large sources of random and systematic errors compared to the analysis itself (Barcelona, 1989). Negative bias (i.e., measured value less than true value) is perhaps the most significant and most difficult to delineate and control. This error is caused primarily by loss through volatilization during soil sample collection, storage, and handling.

TABLE 1. RANKING OF GROUND WATER CONTAMINANTS BASED ON FREQUENCY OF DETECTION AT 358 HAZARDOUS WASTE DISPOSAL SITES

Contaminant	Detection Frequency
Trichloroethene (V)	51.3
Tetrachloroethene (V)	36.0
1,2-trans Dichloroethene (V)	29.1
Chloroform (V)	28.4
1,1-Dichloroethene (V)	25.2
Methylene chloride (V)	19.2
1,1,1-Trichloroethane (V)	18.9
1,1-Dichloroethane (V)	17.9
1,2-Dichloroethane (V)	14.2
Phenol (A)	13.6
Acetone (V)	12.4
Toluene (V)	11.6
bis-(2-Ethylhexyl) phthalate (B)	11.5
Benzene (V)	11.2
Vinyl chloride	8.7

V = volatile, A = acid extractable, B = base/neutral
Source: Plumb and Pitchford (1985).

There are currently no standard procedures for sampling soils for VOC analyses. Several types of samplers are available for collecting intact (undisturbed) samples and bulk (disturbed) samples. The selection of a particular device is site-specific. Samples are usually removed from the sampler and are placed in glass jars or vials that are then sealed with Teflon-lined caps. Practical experience and recent field and laboratory research, however, suggest that procedures such as these may lead to significant VOC losses (losses that would affect the utility of the data). Hanisch and McDevitt (1984) reported that any headspace present in the sample container will lead to desorption of VOCs from the soil particles into the headspace and will cause loss of VOCs upon opening of the container. Siegrist and Jennsen (1990) found that 81% of the VOCs were lost from samples containerized in glass jars sealed with Teflon-lined caps compared to samples immersed in methanol in jars.

FACTORS AFFECTING VOC RETENTION AND CONCENTRATION IN SOIL SYSTEMS

Volatile organic compounds in soil may coexist in three phases: gaseous, liquid (dissolved), and solid (sorbed). [Note: "Sorbed" is used throughout this paper to encompass physical and chemical adsorption and phase partitioning.] The sampling, identification, and quantitation of VOCs in soil matrices are complicated because VOC molecules can coexist in these three phases. The interactions between these phases are illustrated in Figure 1. The phase distribution is controlled by VOC physicochemical properties (e.g., solubility, Henry's constant), soil properties, and environmental variables (e.g., soil temperature, water content, organic carbon content).

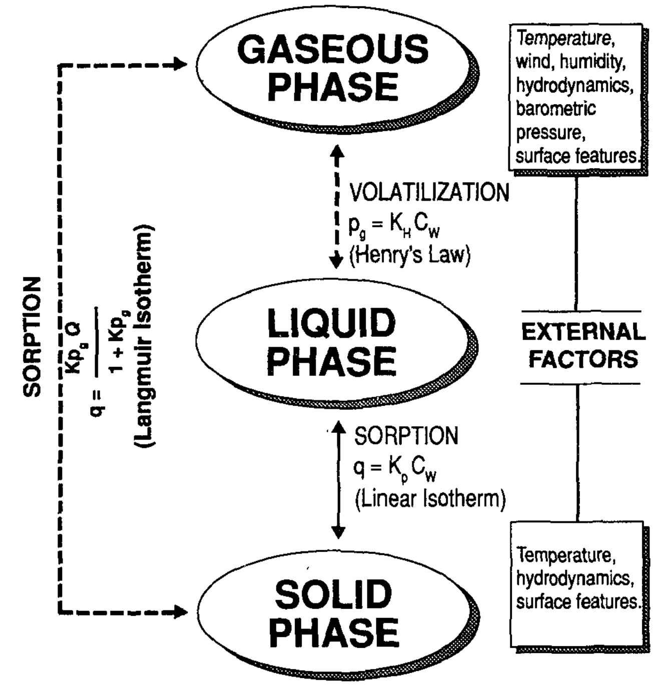

Figure 1. Equilibrium relationships for phase partitioning of VOCs in soil systems. See Table 2 for definitions of abbreviations.

The factors that affect the concentration and retention of VOCs in soils can be divided into five categories: VOC chemical properties, soil chemical properties, soil physical properties, environmental factors, and biological factors. A brief summary of VOC, soil, and environmental factors is presented in Table 2, which provides an overview of the factors that interact to control VOCs in the soil environment at the time a sample is collected. The cited references provide a more detailed discussion. The chemical and physical properties of selected VOCs are further described in Table 3. Note that many of these properties have been determined in the laboratory under conditions (e.g., temperature, pressure) that may differ from those encountered in the field. Devitt et al. (1987) offers a more exhaustive list.

Many VOCs exhibit extreme mobilities, particularly in the vapor phase, where their gas diffusion coefficients can be four times greater than their liquid diffusion coefficients. The vapor phase migration is influenced by the moisture content of the soil which alters the air-filled to water-filled pore volume ratio. The retention of VOCs by soil is largely controlled by reactions with the solid phase. This retention is especially true for the finer particles of silts and clays. The fine-grained particles (<2 mm) have a large surface-to-volume ratio, a large number of reactive sites, and high sorption capacities (Richardson and Epstein, 1971; Boucher and Lee, 1972; Lotse et al., 1968). Some investigators attribute the greater sorption of VOCs onto fine-grained particles to the greater organic carbon content of smaller particles (Karickhoff et al., 1979).

Soil-moisture content affects the relative contributions of mineral and organic soil fractions to the retention of VOCs (Smith et al., 1990). Mineral clay surfaces largely control sorption when soil moisture is extremely low (<1%), and organic carbon

(Continued on page 7)

TABLE 2. FACTORS AFFECTING VOC CONCENTRATIONS IN SOILS

Factor	Common Abbr.	Units	Effects on VOC Concentrations in Soil	References
VOC Chemical Properties				
Solubility	C_w	mg/L	Affects fate and transport in water, effects water/air partit., influences organic carbon partit.	Roy and Griffin (1985)
Henry's Constant	K_H	(atm-m^3)/mole	Constant of proportionality between the water and gas phase concentrations; temperature and pressure dependent.	Shen and Sewell (1982) Spencer et al. (1988)
Vapor pressure	v.p.	mm Hg	Affects rate of loss from soil.	Shen and Sewell (1982)
Organic carbon part. coeff.	K_{oc}	mg VOC/g C	Adsorption coefficient normalized for soil organic content.	Farmer et al. (1980)
Octanol/water part. coeff.	K_{ow}	mg VOC/ mg octanol	Equilibrium constant for distribution of VOC between water and an organic (octanol) phase. Gives estimate of VOC partitioning into organic fraction of soil.	Voice and Weber (1983)
Boiling point	b.p.	°C	Affects co-evaporation of VOC and water from soil surface.	Voice and Weber (1983)
Soil/water distribution coefficient	K_d	[1]	Equilibrium constant for distribution of contaminant between solid and liquid phases.	Voice and Weber (1983)

(Continued)

TABLE 2. (CONTINUED)

Factor	Common Abbr.	Units	Effects on VOC Concentrations in Soil	References
Soil Chemical Properties				
Cation exchange capacity	CEC	meq/100 g	Estimates the number of negatively charged sites on soil particles where charged VOC may sorb; pH dependent.	
Ion concentration (activity)	pH	-log[H^+]	Influences a number of soil processes that involve non-neutral organic partitioning; affects CEC and solubility of some VOCs.	
Total organic carbon content	TOC	mg C/g soil	An important partitioning medium for non-polar, hydrophobic (high K_{oc}) VOCs; sorption of VOCs in this medium may be highly irreversible.	Chiou et al. (1988) Farmer et al. (1980)
Soil Physical Properties				
Particle size or texture	A	% sand, silt, clay	Affects infiltration, penetration, retention, sorption, and mobility of VOCs. Influences hydraulics as well as surface-area-to-volume ratio (s.a.$\propto$Kd).	Richardson and Epstein (1971)
Specific surface area	s.a.	m^2/g	Affects adsorption of VOCs from vapor phase; affects soil porosity and other textural properties.	Karickhoff et al. (1979)
Bulk density	p_b	g/cm^3	Used in estimating mobility and retention of VOCs in soils; will influence soil sampling device selection.	Spencer et al. (1988)
Porosity	n	%	Void volume to total volume ratio. Affects volume, concentration, retention, and migration of VOCs in soil voids.	Farmer et al. (1980) Shen and Sewell (1982)
Percent moisture	Θ	% (w/w)	Affects hydraulic conductivity of soil and sorption of VOCs. Determines the dissolution and mobility of VOCs in soil.	Farmer et al. (1980) Chiou and Shoup (1985)
Water potential	pF	m	Relates to the rate, mobility, and concentration of VOCs in water or liquid chemicals.	
Hydraulic conductivity	K	m/d	Affects viscous flow of VOCs in soil water depending on degree of saturation, gradients, and other physical factors.	
Environmental Factors				
Relative humidity	R.H.	%	Could affect the movement, diffusion, and concentration of VOCs; interrelated factors; could be site specific and dependent upon soil surface - air interface differentials.	Chiou and Shoup (1985)
Temperature	T	°C		
Barometric pressure		mm Hg		
Wind speed		knots	Relevant to speed, movement, and concentration of VOCs exposed, removed, or diffusing from soil surface.	
Ground cover		%	Intensity, nature, and kind, and distribution of cover could affect movement, diffusion rates, and concentration of VOCs.	

TABLE 3. CHEMICAL PROPERTIES OF SELECTED VOLATILE ORGANIC COMPOUNDS†

Compound	m.w. (g/mole)	Solubilities (mg/L @ 20°C)	log K_{oc} [a]	log K_{ow} [b]	K_H [c]	Vapor Pressure (mm @ 20°C)
Acetone	58	Miscible		-0.22	-0.24	270 (@ 30°)
Benzene	78	1780	1.91	2.11	0.22	76
Bromodichloromethane	164	7500	2.18	2.10		50
Bromoform	253	3190 (@ 30°)				6 (@ 25°)
Bromomethane	95	900	1.34	1.19	1.50	1250
2-Butanone	72	270000	1.56	0.26		76
Carbon disulfide	76	2300	1.80			260
Carbon tetrachloride	154	800	2.04	2.64	0.94	90
Chlorobenzene	113	500	2.18	2.84	0.16	9
Chloroethane	65	5740	1.40	1.54	0.61	1000
2-Chloroethylvinyl ether	107					
Chloroform	120	8000	1.46	1.97	0.12	160
Chloromethane	51	8348	0.78	0.91	1.62	3800
Dibromochloromethane	208	3300	2.45	2.24		15 (@10.5°)
1,2-Dichlorobenzene	147	100	2.62	3.38		1
1,3-Dichlorobenzene	147	123 (@ 25°)		3.38		
1,4-Dichlorobenzene	147	49 (@ 22°)		3.39		1
1,1-Dichloroethane	99	5500	1.66	1.79	0.18	180
1,2-Dichloroethane	99	8690	1.34	1.48	0.04	61
1,1-Dichloroethene	97	400				500
trans-1,2-Dichloroethene	97	600	1.56	2.06		200 (@ 14°)
1,2-Dichloropropane	113	2700		1.99		42
cis-1,3-Dichloropropene	110	2700				34 (@ 25°)
trans-1,3,-Dichloropropene	111	2800				43 (@ 25°)
Ethylbenzene	106	152	2.60	3.15		7
2-Hexanone	100	3500		1.38		2
Methylene chloride	85	20000	1.40	1.25		349
Methylisobutylketone	100	17000	1.34	1.46	0.002	6
Perchloroethylene	166	150	2.60	2.60	0.85	14
Styrene	104	300	2.61	2.95		5
1,1,2,2-Tetrachloroethane	168	2900	2.07	2.60		5
Tetrachloroethene	166	150	2.78	3.40		18 (@ 25°)
Toluene	92	515	2.18	2.69	0.27	22
1,1,1-Trichloroethane	133	4400	2.19	2.50	1.46	100
1,1,2-Trichloroethane	133	4500	2.14	2.07		19
Trichloroethylene	132	700	2.09	2.29	0.37	60
Trichlorofluoromethane	137	1100 (@ 25°)	2.68			687
Vinyl acetate	86	25000	1.59	0.73		115 (@ 25°)
Vinyl chloride	63	1100 (@ 25°)	2.60	1.38	97.0	2660 (@ 25°)
Total xylenes	106	198	2.46		9400.0	

† From Verschueren 1983, Jury 1984.
[a] Organic carbon partitioning coefficient.
[b] Octanol/water partitioning coefficient.
[c] Henry's Gas Law constant (dimensionless) @ 20°C.

TABLE 4. MICROBIOLOGICAL FACTORS AFFECTING VOCs IN SOIL SYSTEMS

Organism(s)	Compound(s)	Conditions	Remarks/metabolite(s)
Various soil microbes	Pentachlorophenol	Aerobic	tetra-, tri-, di-, and m-Chlorophenol (Kobayashi and Rittman, 1982)
	1,2,3- and 1,2,4-Trichlorobenzene	Aerobic	2,6-; 2,3-Dichlorobenzene; 2,4- and 2,5-dichlorobenzene; CO_2 (Kobayashi and Rittman, 1982)
Various soil bacteria	Trichloroethane, trichloromethane, methylchloride, chloroethane, dichloroethane, vinylidiene chloride, trichloroethene, tetrachloroethene, methylene chloride, dibromochloromethane, bromochloromethane	Anaerobic	Reductive dehalogenation under anoxic conditions, (i.e., < 0.35 V) (Kobayashi and Rittman, 1982)
Various soil microbes	Tetrachloroethene	Anaerobic	Reductive dehalogenation to trichloroethene,dichloroethene, and vinyl chloride, and finally CO_2 (Vogel and McCarty, 1985)
Various soil microbes	^{13}C-labeled trichloroethene	Anaerobic	Dehalogenation to 1,2-dichloroethene and not 1,1-dichloroethene (Kleopfer et al., 1985)
Various soil bacteria	Trichloroethene	Aerobic	Mineralized to CO_2 in the presence of a mixture of natural gas and air
Actinomycetes	chlorinated and non-chlorinated aromatics	aerobic	Various particle breakdown products mineralized by other microorganisms (Lechevalier and Lechevalier, 1976)
Fungi	DDT	Aerobic	Complete mineralization in 10-14 days (Johnsen, 1976)
Pseudomonas sp. *Acinetobacter* sp. *Micrococcus* sp.	Aromatics	Aerobic	Organisms were capable of sustaining growth in these compounds with 100% biodegradation (Jamison et al., 1975)
Acetate-grown biofilm	Chlorinated aliphatics	Aerobic	No biodegration observed (Bouwer, 1984)
		Methanogenic	Nearly 100% biodegradation observed (Bouwer, 1984)
	Chlorinated and nonchlorinated aromatics	Aerobic	Nearly 100% biodegradation (Bouwer, 1984)
		Methanogenic	No biodegration observed (Bouwer, 1984)
Blue-green algae (cyanobacteria)	Oil wastes	Aerobic	Biodegradation of automobile oil wastes, crankcase oil, etc. (Cameron, 1963)

partitioning is favored when moisture content is higher (Chiou and Shoup, 1985).

Biological factors affecting VOC retention in soil systems can be divided into microbiological and macrobiological factors. On the microbiological level, the indigenous microbial populations present in soil systems can alter VOC concentrations. Although plants and animals metabolize a diversity of chemicals, the activities of the higher organisms are often minor compared to the transformations affected by heterotrophic bacteria and fungi residing in the same habitat. The interactions between environmental factors, such as dissolved oxygen, oxidation-reduction potential (Eh), temperature, pH, availability of other compounds, salinity, particulate matter, and competing organisms, often control biodegradation. The physical and chemical characteristics of the VOC, such as solubility, volatility, hydrophobicity, and K_{ow}, also influence the ability of the compound to biodegrade. Table 4 illustrates some examples of the microbiological alterations of some commonly encountered soil VOCs. In general, the halogenated alkanes and alkenes are metabolized by soil microbes under anaerobic conditions (Kobayashi and Rittman, 1982; Bouwer, 1984), whereas the halogenated aromatics are metabolized under aerobic conditions. To avoid biodegradation and oxidation of VOCs in soils, scientists at the U.S. EPA Robert S. Kerr Environmental Research Laboratory in Ada, OK, extrude the sample in a glove box.

On a macro scale, biological factors can influence the migration of VOCs in the saturated, vadose, and surface zones (Table 5). Biofilms may accumulate in the saturated zone and may biodegrade and bioaccumulate VOCs from the ground water. The biofilm, depending on its thickness, may impede ground-water flow. Plant roots have a complex microflora associated with them known as mycorrhizae. The mycorrhizae may enhance VOC retention in the soil by biodegradation or bioaccumulation. The root channels may act as conduits for increasing the migration of VOCs through the soil. Similarly, animal burrows and holes may serve as paths of least resistance for the movement of VOCs through soil. These holes may range from capillary-size openings, created by worms and nematodes, to large-diameter tunnels excavated by burrowing animals. These openings may increase the depth to which surface spills penetrate the soil. A surface covering consisting of assorted vegetation is a significant barrier to volatilization of VOCs into the atmosphere. Some ground-water and vadose-zone models (e.g., RUSTIC) include subroutines to account for a vegetative cover (Dean et al., 1989).

TABLE 5. MACROBIOLOGICAL FACTORS AFFECTING VOCs IN SOIL SYSTEMS

Factor	Zone	Effects
Biofilms	Saturated	Biodegradation, bioaccumulation, formation of metabolites that are more or less toxic than parent compound, thick biofilm may retard saturated flow
Plant roots	Capillary fringe to vadose	Mycorrihizal fungi may biodegrade or bioaccumulate VOC, root channels may serve as conduits for VOC migration
Animal burrows holes	Vadose	May act as entry point for and downward migration of surface spills and serve as conduit for upward VOC migration
Vegetative cover	Soil surface	Serve as barrier to volatilization from soil surface and retard infiltration of surface spills

SOIL SAMPLING AND ANALYSIS DESIGN

Prior to any sampling effort, the RPM or OSC must establish the intended purpose of the remedial investigation/feasibility study (RI/FS). The goals of collecting samples for VOA may include source identification, spill delineation, fate and transport, risk assessment, enforcement, remediation, or post-remediation confirmation. The intended purpose of the sampling effort drives the selection of the appropriate sampling approach and the devices to be used in the investigation.

The phase partitioning of the VOC can also influence which sampling device should be employed. Computer models generally are used only at the final stages of a RI/FS. However, modeling techniques can be used throughout the RI/FS process to assist in sampling device selection by estimating the phase partitioning of VOCs. The RPM is the primary data user for a RI/FS led by a federal agency. As such, the RPM must select the sampling methodology to be employed at the site. Figure 2 illustrates the sequence of events used to plan a VOC sampling and analysis activity.

The domains of interest also must be determined. The target domains may include surface (two dimensions) or subsurface (three dimensions) environments, hot spots, a concentration greater or less than an action limit, or the area above a leaking underground storage tank. Statistics that may be generated from the target domain data must be considered before a sample and analysis design is developed. Possible statistics of interest may include average analyte concentration and the variance about the mean (statistics that compare whether the observed level is significantly above or below an action level) as well as temporal and spatial trends. Data must be of sufficiently high quality to meet the goals of the sampling activity. The level of data quality is defined by the data quality objectives (DQOs). In RI/FS activities, sites are so different and information on overall measurement error (sampling plus analytical error) is so limited that it is not practical to set universal or generic precision, accuracy, representativeness, completeness, and comparability (PARCC) goals. The reader is referred to a user's guide on quality assurance in soil sampling (Barth et al., 1989) and a guidance document for the development of data quality objectives for remedial response activities (U.S. EPA, 1987).

DQOs are qualitative and quantitative statements of the level of uncertainty a decision maker is willing to accept in making decisions on the basis of environmental data. It is important to realize that if the error associated with the sample collection or

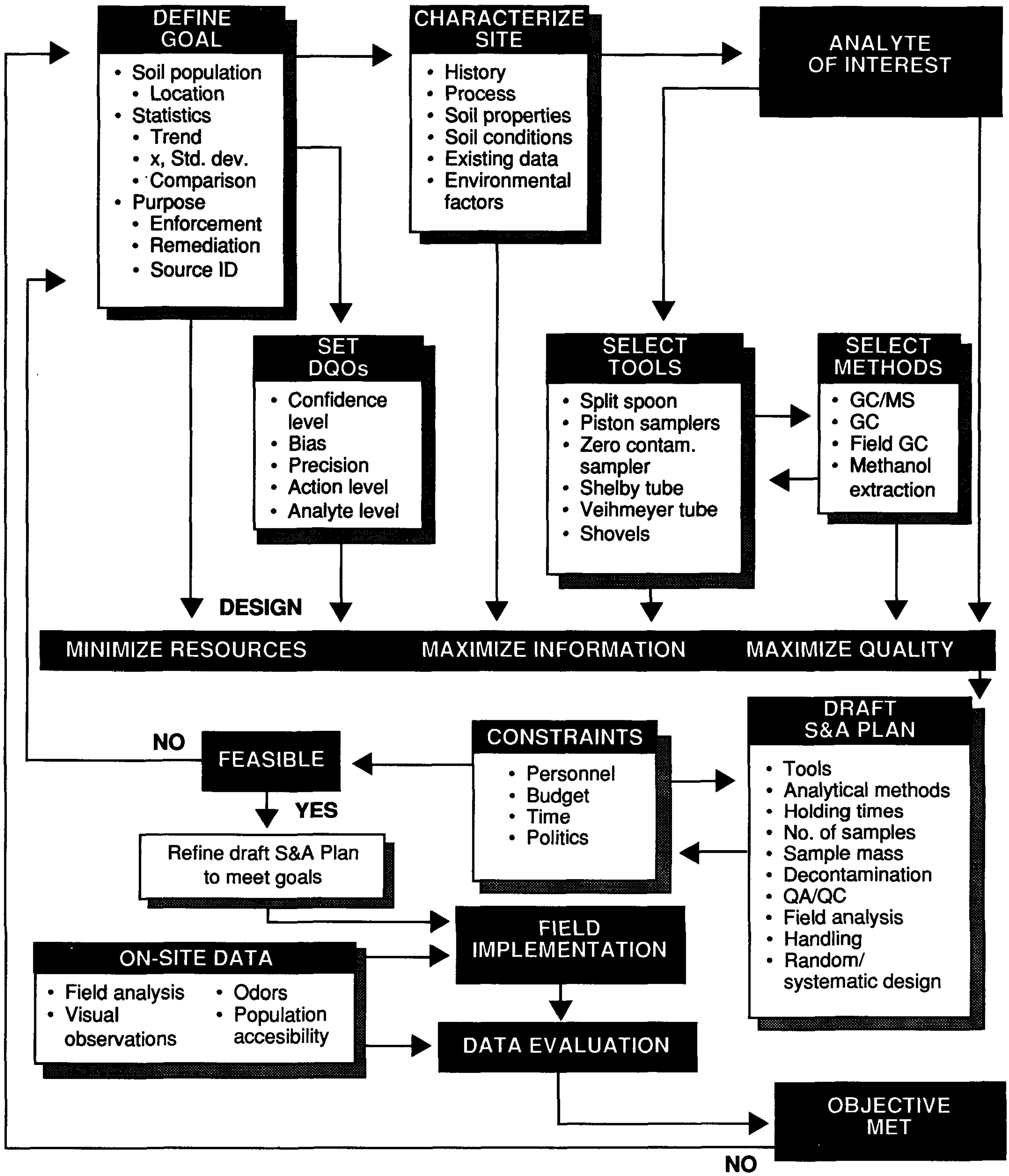

Figure 2. Flowchart for planning and implementation of a soil sampling and analysis activity.

preparation step is large, then the best laboratory quality assurance program will be inadequate (van Ee et al., 1990). The greatest emphasis should be placed on the phase that contributes the largest component of error. For the analysis of soils for VOCs, the greatest sources of error are the sample collection and handling phases.

The minimum confidence level (CL) required to make a decision from the data is defined by the DQOs. The minimum CL depends on the precision and accuracy in sampling and analysis and on the relative analyte concentration. Relative error may be reduced by increasing either the number or the mass of the samples to be analyzed. For instance, although 5-g aliquots collected in the field might exhibit unacceptable errors, 100-g samples will yield smaller errors and might therefore meet study or project requirements. Compositing soil samples in methanol in the field also can reduce variance by attenuating short-range spatial variability.

Field sampling personnel should coordinate with laboratory analysts to ensure that samples of a size appropriate to the analytical method are collected. For example, if the laboratory procedure for preparing aliquots calls for removing a 5-g aliquot from a 125-mL wide-mouth jar, as per SW-846, Method 8240 (U.S. EPA 1986b), then collecting a larger sample in the field will not reduce total measurement error, because additional errors will be contributed from opening the container in the laboratory and from subsequent homogenization. Aliquoting of a 5-g sample in the field into a 40-mL VOA vial that can be directly attached to the laboratory purge-and-trap unit significantly reduces loss of VOCs from the sample (U.S. EPA, 1991a). Significant losses of VOCs were observed when samples were homogenized as per Method 8240 specifications. Smaller losses were observed for smaller aliquots (1 to 5 g) placed in 40-mL VOA vials that had modified caps that allowed direct attachment to the purge-and-trap device. The procedure of collecting an aliquot in the field eliminates the need for sample preparation and eliminates subsequent VOC loss in the laboratory.

Field-screening procedures are gaining recognition as an effective means of locating sampling locations and obtaining real-time data. The benefits of soil field-screening procedures are: (1) near real-time data to guide sampling activities, (2) concentration of Contract Laboratory Program (CLP) sample collection in critical areas, (3) reduced need for a second visit to the site, and (4) reduced analytical load on the laboratory. Limitations of field-screening procedures are: (1) a priori knowledge of VOCs present at the site is needed to accurately identify the compounds, (2) methodologies and instruments are in their infancy and procedures for their use are not well documented and (3) a more stringent level of quality assurance and quality control (QA/QC) must be employed to ensure accurate and precise measurements. The potential benefits and limitations associated with soil-screening procedures must be carefully weighed and compared to the DQOs.

Certain sampling and analytical methods have inherent limitations on the type of QA/QC that is applicable. For example, splitting soil samples in the field would not be appropriate for VOA due to excessive analyte loss. The higher the minimum CL needed to make a decision, the more rigorous the QA/QC protocols must be. As VOC concentrations in the soil sample approach the action or detection limit, the quantity and frequency of QA/QC samples must be increased, or the number of samples must be increased, to ensure that the data quality obtained is appropriate to satisfy project objectives.

One critical element in VOC analysis is the appropriate use of trip blanks. If a sample consists of a silty clay loam, a trip blank of washed sand may not be realistic, for such a blank would not retain VOC cross contaminants in the same way as the sample. The trip blank soil matrix should have a sorptive capacity similar to the actual sample. In addition, high-concentration and low-concentration samples should be shipped in separate coolers.

DEVICE SELECTION CRITERIA

The selection of a sampling device and sampling procedures requires the consideration of many factors including the number of samples to be collected, available funds, soil characteristics, site limitations, ability to sample the target domain, whether or not screening procedures are to be used, the size of sample needed, and the required precision and accuracy as given in the DQOs. The number of samples to be collected can greatly affect sampling costs and the time required to complete a site characterization. If many subsurface samples are needed, it may be possible to use soil-gas sampling coupled with on-site analysis as an integrated screening technique to reduce the area of interest and thus the number of samples needed. Such a sampling approach may be applicable for cases of near-surface contamination.

Ultimately, the sampling, sample handling, containerizing, and transport of the soil sample should minimize losses of volatiles and should avoid contamination of the sample. Soil sampling equipment should be readily decontaminated in the field if it is to be reused on the job site. Decontamination of sampling equipment may require the use of decontamination pads that have impervious liners, wash and rinse troughs, and careful handling of large equipment. Whenever possible, a liner should be used inside the sampling device to reduce potential cross contamination and carryover. Decontamination procedures take time, require extra equipment, and ultimately increase site characterization costs. Ease and cost of decontamination are thus important factors to be considered in device selection.

Several soil-screening procedures are in use that include headspace analysis of soils using organic vapor analyzers: water (or NaCl-saturated water) extraction of soil, followed by static headspace analysis using an organic vapor analyzer (OVA) or gas chromatograph (GC); colorimetric test kits; methanol extraction followed by headspace analysis or direct injection into a GC; and soil-gas sampling (U.S. EPA, 1988). Field measurements may not provide absolute values but often may be a superior means of obtaining relative values. These procedures are gaining acceptance.

Site Characteristics

The remoteness of a site and the physical setting may restrict access and, therefore, affect equipment selection. Such factors as vegetation, steep slopes, rugged or rocky terrain, overhead power lines or other overhead restrictions, and lack of roads can contribute to access problems.

The presence of underground utilities, pipes, electrical lines, tanks and leach fields can also affect selection of sampling equipment. If the location or absence of these hazards cannot be established, it is desirable to conduct a nonintrusive survey of the area and select a sampling approach that minimizes hazards. For example, hand tools and a backhoe are more practical under such circumstances than a large, hollow-stem auger. The selection of a sampling device may be influenced by other contaminants of interest such as pesticides, metals, semivolatile organic compounds, radionuclides, and explosives. Where the site history indicates that the matrix is other than soil, special consideration should be given to device selection. Concrete, reinforcement bars, scrap metal, and lumber will affect sampling device selection. Under some circumstances, it may not be practical to collect deep soil samples. The presence of ordnance, drums, concrete, voids, pyrophoric materials, and high-hazard radioactive materials may preclude some sampling and may require development of alternate sampling designs, or even reconsideration of project objectives.

Soil Characteristics

The characteristics of the soil material being sampled have a marked effect upon the selection of a sampling device. An investigator must evaluate soil characteristics, the type of VOC, and the depth at which a sample is to be collected before selection of a proper sampling device. Specific characteristics that must be considered are:

1. Is the soil compacted, rocky, or rubble filled? If the answer is yes, then either hollow stem augers or pit sampling must be used.

2. Is the soil fine grained? If yes, use split spoons, Shelby tubes, liners, or hollow stem augers.

3. Are there flowing sands or water saturated soils? If yes, use samplers such as piston samplers that can retain these materials.

SOIL-GAS MEASUREMENTS

Soil-gas measurements can serve a variety of screening purposes in soil sampling and analysis programs, from initial site reconnaissance to remedial monitoring efforts. Soil-gas measurements should be used for screening purposes only, and not for definitive determination of soil-bound VOCs. Field analysis is usually by hand-held detectors, portable GC or GC/MS, infrared detectors, ion mobility spectrometers (IMS), industrial hygiene detector tubes, and, recently, fiber optic sensors.

At some sites, soil-gas sampling may be the only means of acquiring data on the presence or absence of VOCs in the soil. For example, when the size and density of rocks and cobbles at a site prevent insertion and withdrawal of the coring device and prevent sampling with shovels and trowels, unacceptable losses of VOCs would occur. Soil-gas measurements, which can be made on site or with collected soil samples, can be used to identify volatile contaminants and to determine relative magnitudes of concentration. Smith et al. (1990) have shown a disparity in soil-gas VOC concentrations and the concentration of VOCs found on the solid phase.

Soil-gas measurements have several applications. These include in situ soil-gas surveying, measurement of headspace concentrations above containerized soil samples, and scanning of soil contained in cores collected from different depths. These applications are summarized in Table 6. Currently, no

TABLE 6. APPLICATIONS OF SOIL-GAS MEASUREMENT TECHNIQUES IN SOIL SAMPLING FOR VOCs

Application	Uses	Methods	Benefits/limitations
Soil vapor surveying	Identify sources and extent of contamination. Distinguish between soil and ground water contamination. Detect VOCs under asphalt, concrete, etc.	Active sampling from soil probes into canisters, glass bulbs, gas sampling bags. Passive sampling onto buried adsorptive substrates. Followed by GC or other analysis.	BENEFITS: Rapid, inexpensive screening of large areas, avoid sampling uncontaminated areas. LIMITATIONS: False positives and negatives, miss detecting localized surface spills, disequilibrium between adsorbed and vapor phase VOC concentrations.
Soil headspace measurements	Screen large numbers of soil samples.	Measure headspace above containerized soil sample. Containers range from plastic sandwich bags to VOA vials. Use GC, vapor detectors, IMS, etc.	BENEFITS: More representative of adsorbed solid phase concentration. LIMITATIONS: Losses of vapor phase component during sampling and sample transfer.
Screening soil cores	Soil cores scanned to locate depth where highest VOC levels are located.	Collect core sample (e.g., unlined split spoon) and scan for vapors near core surface using portable vapor monitor.	BENEFITS: Locate and collect soil from hot spot in core for worst case. LIMITATIONS: False negatives and positives, environmental conditions can influence readings (e.g., wind speed and direction, temperature, humidity).

standard protocols exist for soil-gas analysis; many investigators have devised their own techniques, which have varying degrees of efficacy. Independently, the American Society for Testing and Materials (ASTM) and EPA EMSL-LV are preparing guidance documents for soil-gas measurement. These documents should be available late in 1991.

The required precision and accuracy of site characterization, as defined in the DQOs, affect the selection of a sampling device. Where maximum precision and accuracy are required, sampling devices that collect an intact core should be used, particularly for more volatile VOCs in nonretentive matrices. Augers and other devices that collect highly disturbed samples and expose the samples to the atmosphere can be used if lower precision and accuracy can be tolerated. Collection of a larger number of samples to characterize a given area, however, can compensate for a less precise sampling approach. The closer the expected contaminant level is to the action or detection limit, the more efficient the sampling device should be for obtaining an accurate measurement.

SOIL SAMPLING DEVICES

Table 7 lists selection criteria for different types of commercially available soil sampling devices based on soil type, moisture status, and power requirements. The sampling device needed to achieve a certain sampling and analysis goal can be located in Table 7 and the supplier of such a device can be identified in Table 8. Table 8 is a partial list of commercially available soil sampling devices that are currently in use for sampling soils for VOC analysis. The list is by no means exhaustive and inclusion

(Continued on page 14)

TABLE 7. CRITERIA FOR SELECTING SOIL SAMPLING EQUIPMENT†

Type of Sampler	Obtains Core Samples	Most Suitable Soil types	Operation in Stony Soils	Suitable Soil Moisture Conditions	Relative Sample Size	Labor Requirements (# of Persons)	Manual or Power Operation
A. Mechanical Sample Recovery							
1. Hand-held Power augers	No	Coh/coh'less	Unfavorable	Intermediate	Large	2+	Power
2. Solid stem flight augers	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
3. Hollow-stem augers	Yes	Coh/coh'less	Fav/unfav	Wet to dry	Large	2+	Power
4. Bucket augers	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
5. Backhoes	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
B. Samplers							
1. Screw-type augers	No	Coh	Unfavorable	Intermediate	Small	Single	Manual
2. Barrel augers							
a. Post-hole augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
b. Dutch augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
c. Regular barrel augers	No	Coh	Unfavorable	Intermediate	Large	Single	Manual
d. Sand augers	No	Coh'less	Unfavorable	Intermediate	Large	Single	Manual
e. Mud augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
3. Tube-type samplers							
a. Soil samplers	Yes	Coh	Unfavorable	Wet to dry	Small	Single	Manual
b. Veihmeyer tubes	Yes	Coh	Unfavorable	Intermediate	Large	Single	Manual
c. Shelby tubes	Yes	Coh	Unfavorable	Intermediate	Large	2+*	Both
d. Ring-lined samplers	Yes	Coh'less	Favorable	Wet to intermediate	Large	2+*	Both
e. Continuous samplers	Yes	Coh	Unfavorable	Wet to dry	Large	2+	Power
f. Piston samplers	Yes	Coh	Unfavorable	Wet	Large	2+*	Both
g. Zero-contamination samplers	Yes	Coh	Unfavorable	Wet to intermediate	Small	2+*	Both
h. Split spoon samplers	Yes	Coh	Unfavorable	Intermediate	Large	2+*	Both
4. Bulk samplers	No	Coh	Favorable	Wet to dry	Large	Single	Manual

† Adapted from U.S. EPA, 1986a.
* All hand-operated versions of samplers, except for continuous samplers, can be worked by one person.
Coh = cohesive.

TABLE 8. EXAMPLES OF COMMERCIALLY AVAILABLE SOIL SAMPLING DEVICES

Manufacturers	Sampling Device	Specifications Length (inches) I.D. (inches) Sampler Material	Liners	Features
Associated Design & Manufacturing Co. 814 North Henry Street Alexandria, VA 22314 703-549-5999	Purge and Trap Soil Sampler	3 0.5 Stainless steel		Will rapidly sample soils for screening by "Low Level" Purge and Trap methods.
Acker Drill Co. P.O. Box 830 Scranton, PA 717-586-2061	Heavy Duty "Lynac" Split Tube Sampler	18 & 24 1-1/2 to 4-1/2 Steel	Brass, stainless	Split tube allows for easy sample removal.
	Dennison Core Barrel	24 & 60 1-7/8 to 6-5/16	Brass	Will remove undisturbed sample from cohesive soils.
AMS Harrison at Oregon Trail American Falls, ID 83211	Core Soil Sampler	2 to 12 1-1/2 to 3 Alloy, stainless	Stainless, plastic aluminum, bronze teflon	Good in all types of soils.
	Dual Purpose Soil Recovery Probe	12, 18 &24 3/4 and 1 4130 Alloy, stainless	Butyrate, Teflon stainless	Adapts to AMS "up & down" hammer attachment. Use with or without liners.
	Soil Recovery Auger	8 to 12 2 & 3 Stainless	Plastic, stainless Teflon, aluminum	Adaptable to AMS extension and cross-handles.
Concord, Inc. 2800 7th Ave. N. Fargo, ND 58102 701-280-1260	Speedy Soil Sampler	48 & 72 3/16 to 3-1/2 Stainless	Acetate	Automated system allows retrieval of 24 in soil sample in 12 sec.
	Zero Contamination Unit Hand-Held Sampler			
CME Central Mine Equip. Co. 6200 North Broadway St. Louis, MO 63147 800-325-8827	Continuous Sampler	60 2-1/2 to 5-3/8 Steel, stainless	Butyrate	May not be suitable in stony soils. Adapts to CMS auger.
	Bearing Head Continuous Sample Tube System	60 2-1/2 Steel, stainless	Butyrate	Versatile system. Adapts to all brands of augers.
Diedrich Drilling Equip. P.O. Box 1670 Laporte, IN 46350 800-348-8809	Heavy Duty Split Tube Sampler	18 & 24 2, 2-1/2, 3 Steel	Brass, plastic stainless, Teflon	Full line of accessories are available.
	Continuous Sampler	60 3, 3-1/2	Brass, plastic stainless, Teflon	Switch-out device easily done.

(Continued)

TABLE 8. (CONTINUED)

Manufactures	Sampling Device	——Specifications—— Length (inches) I.D. (inches) Sampler Material	Liners	Features
Geoprobe Systems 607 Barney St. Salina, KS 913-825-1842	Probe Drive Soil Sampler	11-1/4 0.96 Alloy steel		Remains completely sealed while pushed to depth in soil.
Giddings Machine Co. P.O. Drawer 2024 Fort Collins, CO 80522 303-485-5586	Coring Tubes	48 & 60 7/8 to 2-3/8 4130 Molychrome	Butyrate	A series of optional 5/8 in slots permit observation of the sample.
JMC Clements and Associates R.R. 1 Box 186 Newton, IA 50208 800-247-6630	Environmentalist's Sub-soil Probe	36 & 48 0.9 Nickel plated	PETG plastic, stainless	Adapts to drop-hammer to penetrate the hardest of soils.
	Zero Contamination Tubes	12, 18 & 24 0.9 Nickel plated	PETG plastic, stainless	Adapts to power probe.
Mobile Drilling Co. 3807 Madison Ave. Indianapolis, IN 46227 800-428-4475	"Lynac" Split Barrel Sampler	18 & 24 1-1/2	Brass, plastic	Adapts to Mobile wireline sampling system.
Solitest, Inc. 66 Albrecht Drive Lake Bluff, IL 800-323-1242	Zero Contamination Sampler	12, 18 & 24 0.9 Chrome plated	Stainless, acetate	Hand sampler good for chemical residue studies.
	Thin Wall Tube Sampler (Shelby)	30 2-1/2, 3, 3-1/2 Steel		Will take undisturbed samples in cohesive soils and clays.
	Split Tube Sampler	24 1-1/2 to 3 Steel	Brass	Forced into soil by jacking, hydraulic pressure or driving. Very popular type of sampler.
	Veihmeyer Soil Sampling Tube	48 & 72 3/4 Steel		Adapts to drop hammer for sampling in all sorts of soils.
Sprague & Henwood, Inc. Scranton, PA 18501 800-344-8506	S & H Split Barrel Sampler	18 & 24 2 to 3-1/2	Brass, plastic	A general all-purpose sampling device designed for driving into material to be sampled.

Note: This list is not exhaustive. Inclusion in this list should not be construed as endorsement for use.

in the list should not be construed as an endorsement for their use.

Commonly, soil samples are obtained from the near surface using shovels, scoops, trowels, and spatulas. These devices can be used to extract soil samples from trenches and pits excavated by back hoes. A precleaned shovel or scoop can be used to expose fresh soil from the face of the test pit. A thin-walled tube or small-diameter, hand-held corer can be used to collect soil from the exposed face. Bulk samplers such as shovels and trowels cause considerable disturbance of the soil and expose the sample to the atmosphere, enhancing loss of VOCs. Siegrist and Jenssen (1990) have shown that sampling procedures that cause the least amount of disturbance provide the greatest VOC recoveries. Therefore, sampling devices that obtain undisturbed soil samples using either hand-held or mechanical devices are recommended. Sampling devices that collect undisturbed samples include split-spoon samplers, ring samplers, continuous samplers, zero-contamination samplers, and Shelby tubes. These sampling devices can be used to collect surface soil samples or they can be used in conjunction with hollow-stem augers to collect subsurface samples. The soil sampling devices discussed above are summarized in Table 9. Devices where the soil samples can be easily and quickly removed and containerized with the least amount of disturbance and exposure to the atmosphere are highly recommended. U.S. EPA (1986a) gives a more detailed discussion on the proper use of drill rigs and sampling devices.

Liners are available for many of the devices listed in Table 9. Liners make soil removal from the coring device much easier and quicker. Liners reduce cross contamination between samples and the need for decontamination of the sampling device. The liner can run the entire length of the core or can be precut into sections of desired length.

When sampling for VOCs, it is critical to avoid interactions between the sample and the liner and between the sample and the sampler. Such interactions may include either adsorption of VOCs from the sample or release of VOCs to the sample. Gillman and O'Hannesin (1990) studied the sorption of six monoaromatic hydrocarbons in ground water samples by seven materials. The hydrocarbons included benzene, toluene, ethylbenzene, and o-, m-, and p-xylene. The materials examined were stainless steel, rigid PVC, flexible PVC, PTFE Teflon, polyvinylidene fluoride, fiberglass, and polyethylene. Stainless steel showed no significant sorption during an 8-week period. All polymer materials sorbed all compounds to some extent. The order of sorption was as follows: rigid PVC < fiberglass < polyvinylidene fluoride < PTFE < polyethylene < flexible PVC. Stainless steel or brass liners should be used since they exhibit the least adsorption of VOCs. Other materials such as PVC or acetate may be used, provided that contact time between the soil and the liner material is kept to a minimum. Stainless steel and brass liners have been sealed with plastic caps or paraffin before shipment to the laboratory for sectioning and analysis. VOC loss can result from permeation through the plastic or paraffin and volatilization through leaks in the seal. Acetate liners are available, but samples should not be held in these liners for any extended period, due to adsorption onto and permeation through the material. Alternatively, the soil can be extruded from the liner, and a portion can be placed into a wide-mouth glass jar. Smaller aliquots can be taken from the center of the precut liner using subcoring devices and the soil plug extruded into VOA vials.

TABLE 9. SOIL SAMPLERS FOR VOC ANALYSIS

Recommended	Not Recommended
Split spoon w/liners	Solid flight liners
Shelby tube (thin wall tubes)	Drilling mud auger
Hollow-stem augers	Air drilling auger
Veihmeyer or King tubes w/liners	Cable tool
	Hand augers
Piston samplers*	Barrel augers
Zero contamination samplers*	Scoop samplers
Probe-drive samplers	Excavating tools, e.g., shovels, backhoes

* May sustain VOC losses if not used with care

TRANSFER OF SOIL SAMPLES FROM DEVICE TO CONTAINER

The sample transfer step is perhaps the most critical and least understood step in the sampling and analysis procedure. The key point in sample transfer, whether in the field or in the laboratory, is to minimize disturbance and the amount of time the sample is exposed to the atmosphere. It is more important to transfer the sample rapidly to the container than to accurately weigh the aliquot which is transferred, or to spend considerable time reducing headspace. Therefore, a combination of a device for obtaining the appropriate mass of sample and placement of the aliquot into a container that can be directly connected to the analytical device in the laboratory is recommended. Several designs are available for obtaining a 5-g aliquot (or other size). Most subcoring devices consist of a plunger/barrel design with an open end. The device shown in Figure 3 was constructed by Associated Design & Manufacturing Company (Alexandria, VA). Other designs include syringes with the tips removed, and cork borers (Table 8). The device is inserted into the sample and an aliquot is withdrawn. The aliquot, which is of a known volume and approximate weight, can then be extruded into a tared 40-mL VOA vial. Routinely, the vial is then sealed with a Teflon-lined septum cap. Teflon, however, may be permeable to VOCs. Aluminum-lined caps are available to reduce losses due to permeation. At the laboratory, the vial must be opened and the contents of the vial must be transferred to a sparger tube. The transfer procedure will result in significant losses of VOCs from the headspace in the vial. The modified purge-and-trap cap shown in Figure 4 eliminates the loss of VOCs due to container opening and sample transfer. The soil is extruded from the subcorer into a tared 40-mL VOA vial and the modified cap is attached in the field. In the laboratory, the vial is attached directly to a purge-and-trap device without ever being opened to the ambient air.

Use of subcoring devices should produce analytical results of increased accuracy. In order to test this hypothesis, an experiment was conducted in which a bulk soil sample was spiked with 800 µg/kg of different VOCs (Maskarinec, 1990). Three aliquots were withdrawn by scooping, and three aliquots were withdrawn by using the sub-corer approach. The results are presented in Table 10. Although neither method produced quantitative recovery, the subcorer approach produced results that were generally

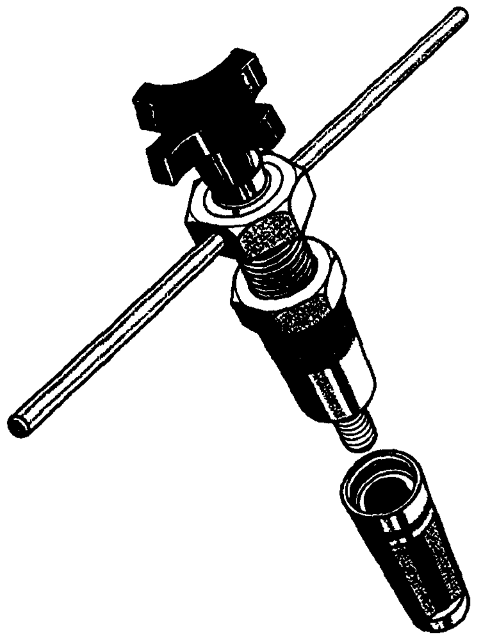

Figure 3. Small-diameter hand-held subcoring device made by Associated Design & Manufacturing Company (Alexandria, VA).

five times higher than the standard approach, whereby the contents of a 125-mL wide-mouth jar are poured into an aluminum tray and homogenized with a stainless steel spatula. A 5-g sample is then placed in the sparger tube (SW-846, Method 8240). Several compounds presented problems with both approaches: styrene polymerizes, bromoform purges poorly, and 1,1,2,2-tetrachloroethane degrades quickly.

TABLE 10. LABORATORY COMPARISON OF STANDARD METHOD AND SUBCORER METHOD

Compound	Standard Method[a]	Subcorer Method[b]	Standard Method % of Recovery of Spike	Subcorer % of Recovery of Spike
Chloromethane	50	1225	6	153
Bromomethane	31	536	4	67
Chloroethane	78	946	10	118
1,1-Dichloroethene	82	655	10	82
1,1-Dichloroethane	171	739	21	92
Chloroform	158	534	20	67
Carbon tetrachloride	125	658	16	82
1,2-Dichloropropane	147	766	18	96
Trichloroethene	120	512	15	64
Benzene	170	636	21	80
1,1,2-Trichloroethane	78	477	10	60
Bromoform	30	170	4	21
1,1,2,2-Trichloroethane	46	271	6	34
Toluene	129	656	16	82
Chlorobenzene	57	298	7	37
Ethylbenzene	68	332	8	42
Styrene	30	191	4	24

[a] µg/kg (n=3)
[b] µg/kg (n=3)
Note: Standard method of sample transfer consists of scooping and subcorer method uses device shown in Figure 3. Soil samples were spiked with 800 µg/kg of each VOC.

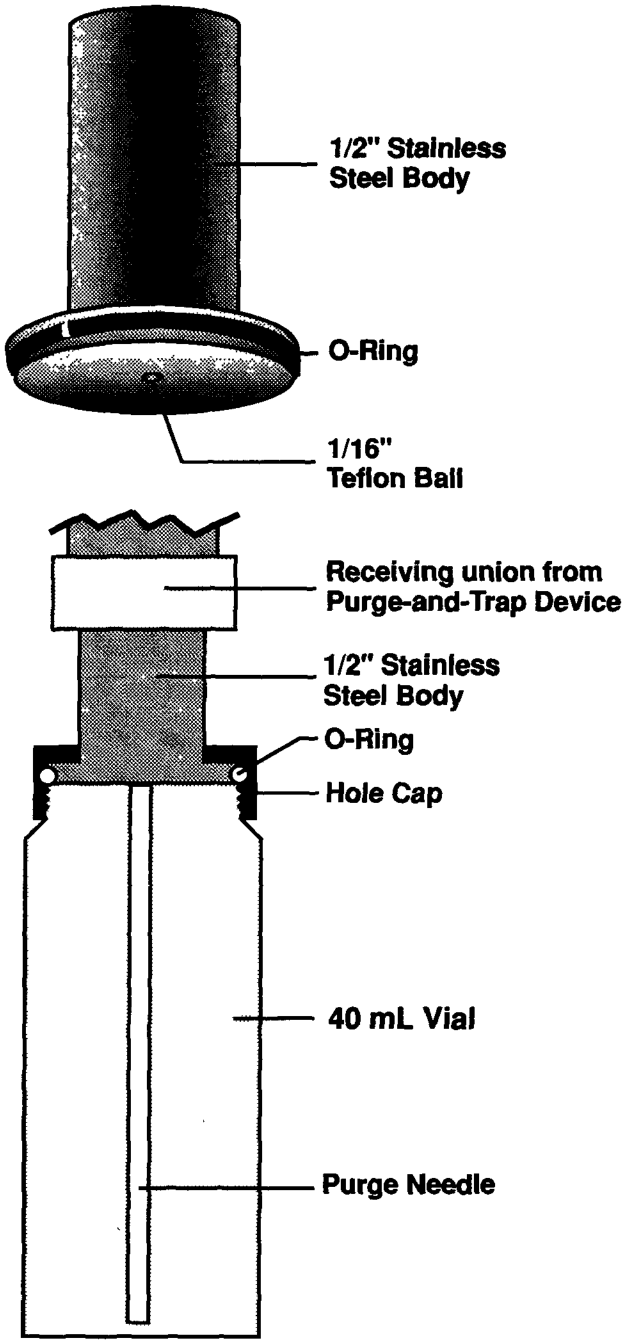

Figure 4. Modified purge-and-trap 40-mL VOA vial cap for containerizing samples in the field. Vial is attached directly to a purge-and-trap system without exposure of sample to the atmosphere.

In another study (U.S. EPA, 1991a), a large quantity of well characterized soil was spiked with 33 VOCs and was homogenized. From the homogenized material, a 5-g aliquot of soil was placed in a 40-mL VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The remaining soil was placed in 125-mL wide-mouth jars. The samples were shipped via air carrier and were analyzed by GC/MS with heated purge and trap. The 40-mL VOA vials were connected directly to a Tekmar purge-and-trap unit without exposure to the atmosphere. The wide-mouth jars were processed as per SW-846 Method 8240 specifications (U.S. EPA, 1986b). Table 11 compares the results of the GC/MS analyses using the two pretreatment techniques. The modified method (40-mL VOA vial with a modified cap) yielded consistently higher VOC concentrations than the traditional Method 8240 procedure (U.S. EPA, 1986b).

The standard methods for VOC analysis, SW-846, Method 8240 and Test Method 624 (U.S. EPA, 1986b; U.S. EPA, 1982), call for the containerizing of soil samples in 40-mL VOA vials or 125-mL wide-mouth jars with minimal headspace. As previously described, wide-mouth jars may not be the most appropriate containers due to sample aliquoting requirements. Although wide-mouth jars may be equally as effective as 40-mL VOA vials in maintaining the VOC content of soil samples, the sample preparation procedure that is required with jar-held samples causes significant (>80%) loss of highly volatile VOCs (Siegrist and Jennsen, 1990). However, if samples are collected in such containers, it is important to ensure sample integrity, preferably by using amber glass jars (for photosensitive compounds) with solid phenolic resin caps and foam-backed Teflon liners. Aluminum-lined caps are not available for the wide-mouth jars. Soil should be wiped from the threads of the jar to ensure a tight seal.

The methanol-immersion procedure calls for the transfer of the sample into a glass jar containing a known volume of chromatographic-grade methanol (usually 100 mL) or in a 1:1 weight-to-volume ratio of soil to methanol. This has the effect of preserving the volatile components of the sample at the time the sample is placed in the container. Furthermore, surrogate compounds can be added at this time in order to identify possible changes in the sample during transport and storage. The addition of methanol to the sample raises the detection limits from 5 to 10 µg/kg to 100 to 500 µg/kg, because of the attendant dilution. However, the resulting data have been shown to be more representative of the original VOC content of the soil (Siegrist and Jennsen, 1990; Siegrist, 1990). In a comparison of transfer techniques, Siegrist and Jennsen (1990) demonstrated that minimum losses were obtained by using an undisturbed sample followed by immediate

TABLE 11. COMPARISON OF VOC CONCENTRATIONS IN SPIKED SOIL ANALYZED BY METHOD 8240 AND MODIFIED METHOD 8240

VOC	Concentration (µg/kg) Method 8240†	Concentration (µg/kg) Modified Method 8240††	Difference	VOC	Concentration (µg/kg) Method 8240†	Concentration (µg/kg) Modified Method 8240††	Difference
Bromomethane	9	44	35**	Dibromochloromethane	121	159	38
Vinyl chloride	3	32	29**	1,1,2-Trichloroethane	142	193	51
Chloroethane	6	36	30**	trans-1,3-Dichloropropene	154	203	49
Methylene chloride	69	100	31**	Bromoform	116	140	24
Carbon disulfide	32	82	50**	Tetrachloroethene	62	124	62**
1,1-Dichloroethene	12	35	23**	1,1,2,2-Tetrachloroethane	137	162	25
1,1-Dichloroethane	34	83	49**	Toluene	85	161	76*
1,2-Dichloroethene	36	66	30**	Chlorobenzene	91	132	41**
Chloroform	56	96	40**	Ethylbenzene	85	135	50**
1,1,1-Trichloroethane	26	80	54**	Styrene	86	114	28*
Carbon tetrachloride	18	61	43**	Total xylenes	57	85	28**
Vinyl acetate	18	26	8				
1,2-Dichloroethane	101	159	58**	KETONES			
cis-1,3-Dichloropropene	136	189	53*	Acetone	336	497	161*
Trichloroethene	48	87	39**	2-Butanone	290	365	75
Benzene	56	114	58*	2-Hexanone	200	215	15
Bromodichloromethane	111	166	55*	4-Methly-2-pentanone	264	288	24

† Method 8240 using 125-mL wide-mouth jar mixing subsampling in laboratory purge/trap analysis.
†† Method 8240 using 40-mL vial. 5-g sampled in the field, shipped to laboratory purge/trap analysis.
** Difference significantly greater than 0, with P-value <0.01.
* Difference significantly greater than 0, with P-value between 0.01 and 0.05.
Note: Spike concentration was 300 µg/kg.

immersion into methanol. The results for six VOCs are shown in Figure 5. At high VOC spike levels (mg/kg) the investigators found that headspace within the bottle caused a decrease in the concentration of VOCs in the sample. At lower spike levels, however, headspace did not seem to be a major contributor to VOC losses (Maskarinec, 1990). In another study (U.S. EPA, 1991a), it was found that a 5-g sample collected from a soil core and placed in a 40-mL VOA vial provided consistently higher

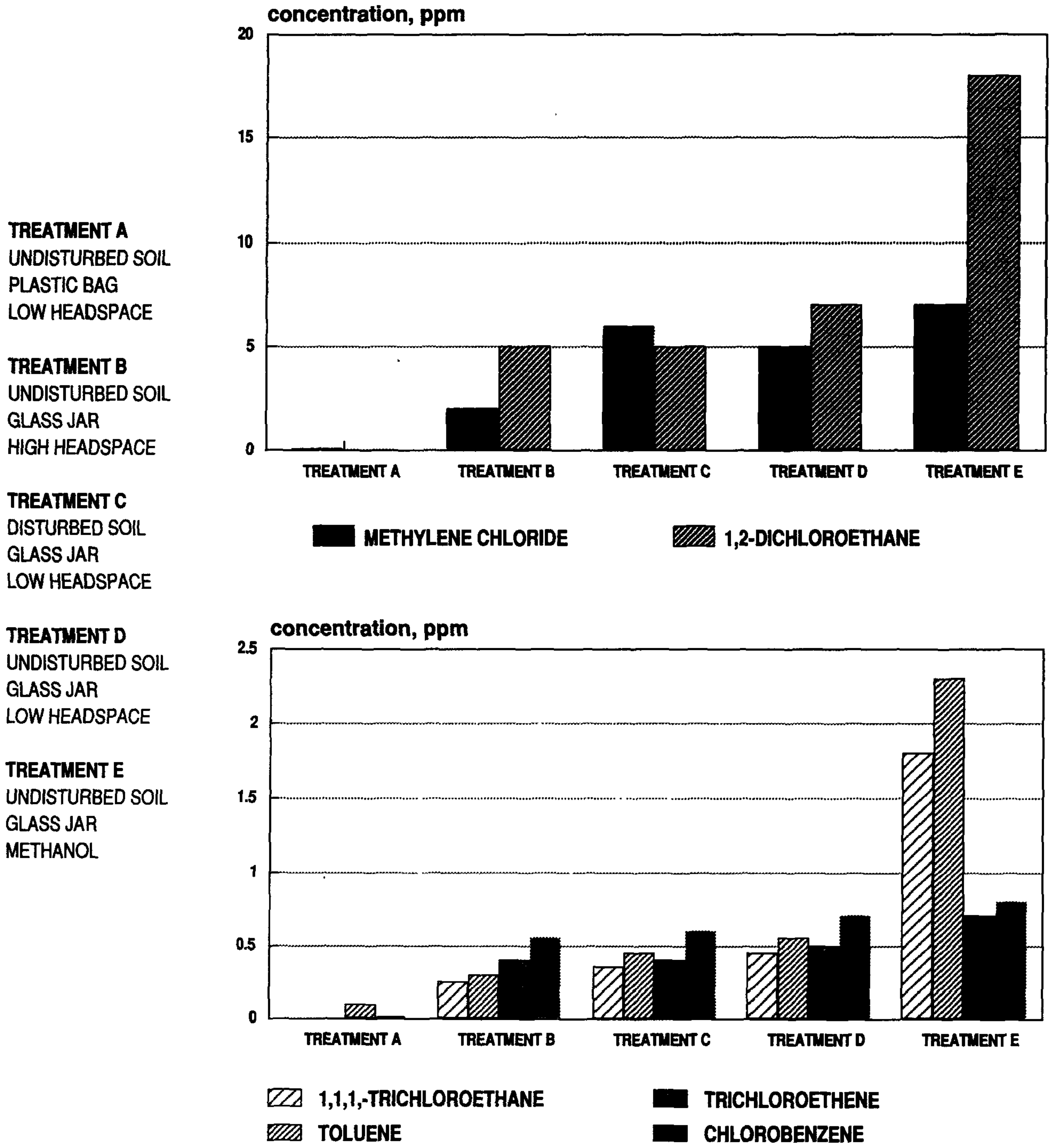

Figure 5. VOC recovery as a function of sample treatment.

VOC levels than a sample taken from the same core, placed in a 125-mL wide-mouth jar, and later poured out, homogenized, and a 5-g aliquot taken from the bulk material as per Method 8240 specifications.

SOIL SAMPLING SCENARIOS

The following recommendations for soil sampling and sample handling are presented for the three general sampling scenarios described earlier.

1. Open Test Pit or Trench

Samples are often collected from exposed test pits or trenches where remediation efforts are in progress. Sites may also be encountered where large-diameter coring devices cannot be employed. In such instances, crude sampling devices, such as trowels, spoons, shovels, spades, scoops, hand augers, or bucket augers must be used to excavate the soil.

The exposed face of an excavated test pit is scraped to uncover fresh material. Samples are collected from the scraped face by using a small-diameter, hand-held corer (Figure 3). If the nominal 5-g sample is to be collected, the appropriate volume (3 to 4 mL) is extruded into a tared 40-mL VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The vial is chilled to 0° to 4°C and sent to the laboratory where the entire contents of the vial are purged without opening the vial (U.S. EPA 1991b). Though this method minimizes losses of VOCs, the small sample size may exhibit greater short-range spatial variability than larger samples.

Alternatively, a small-diameter, hand-held soil corer (Figure 3) can be used to collect a larger volume of soil. The soil is extruded to fill a 40-mL VOA vial with a Teflon-lined septum cap (minimal headspace), chilled, and sent to the laboratory. The major weakness with this method is that VOCs are lost in the laboratory during sample homogenization, preparation of aliquots from a subsample, and the transfer to the extraction or sparging device.

If large coarse fragments or highly compacted soils are encountered, the use of a hand-held corer may not be possible. In this case crude sampling devices are used to rapidly collect and fill (minimal headspace) a 125- or 250-mL wide-mouth glass jar. The threads are wiped clean and the jar is sealed with a foam-backed Teflon-lined cap. The jar is chilled immediately to 0° to 4°C for shipment to the laboratory. Losses of VOCs are considerably greater with this method due to disruption of the matrix and losses in the laboratory during sample preparation. Methanol immersion may be more suitable for these matrices.

2. Surface Soils (< 5 ft deep)

The preferred soil sampling procedures reduce VOC losses by minimizing sample disturbance during collection and transfer to a container. The collection of soil cores with direct extrusion into a container accomplishes this goal. A larger-diameter coring device (e.g., split-spoon sampler, Shelby tube, zero-contamination sampler) is used to collect an intact sample from the surface soil or from an augered hole. Many of these samplers can be used with liners, an insert that greatly reduces the time required to remove the soil and obtain a subsample. For subsamples collected from split spoons or extruded large-diameter cores, the section to be subsampled is scraped and laterally subcored, or the extruded soil is cut or broken to expose fresh material at the depth or zone of interest, then longitudinally subcored. For large-diameter cores that are collected in precut liners, the liner sections are separated with a stainless steel spatula, and a small-diameter hand-held corer is used to collect a subsample from the center of the liner section. The uppermost portion of the core should not be sampled, because it is more likely to be cross contaminated. The small diameter corer (Figure 3) is pushed into the soil, the outside of the corer is wiped clean, and the required core volume (typically about 3 to 4 mL or 5 g) is extruded directly into a tared 40-mL glass VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The vial threads and lip must be free of soil to ensure an airtight seal.

3. Subsurface soils (> 5 ft deep)

The same sampling principles apply for the collection of deeper soil samples. Collection of soil cores with direct extrusion into a container greatly reduces the loss of VOCs. Tube-type samplers such as split-spoon, Shelby tubes, and zero-contamination samplers are used inside a hollow-stem auger to obtain an intact sample from greater depths. The coring device is retrieved and a subsample is obtained in a similar manner as that described for surface soils.

METHANOL IMMERSION PROCEDURE

Soil collected by protocols outlined above can be placed in a tared wide-mouth glass jar containing pesticide-grade methanol (1:1 weight-to-volume ratio of soil to methanol). The immersion of relatively large soil samples into methanol has the advantage of extracting a much larger sample that is probably less prone to short-range spatial variability. This is of particular advantage with coarse-grained soils, materials from which it is hard to obtain a 1-g to 5-g subsample for analysis.

Multiple small-diameter corers can be immersed in a single methanol-filled jar to produce a composite sample. Compositing becomes practical because VOCs are soluble in methanol, thus reducing losses. Appropriately collected composite samples can produce more representative data than a comparable number of individual samples. Short-range spatial variability is greatly reduced. Another advantage is the ability to reanalyze samples. The main disadvantages of using methanol include the requirements for handling and shipping the methanol and the detection limit that is raised by a factor of about 10 to 20. For the methanol-immersion procedure, jars filled with methanol and shipped to the laboratory are classified as a hazardous material, flammable liquid and must be labelled as per Department of Transportation specifications (49 CFR, 1982). If these disadvantages are unacceptable, then the modified purge-and-trap procedure may be applicable.

FIELD STORAGE

Material containing VOCs should be kept away from the sample and the sample container. Hand lotion, labeling tape, adhesives, and ink from waterproof pens contain VOCs that are often analytes of interest in the sample. Samples and storage containers should be kept away from vehicle and generator exhaust and other sources of VOCs. Any source of VOCs may cause contamination that may compromise the resulting data.

Once samples are removed from the sampling device and placed in the appropriate storage container, the containers should be placed in the dark at reduced temperatures (0° to 4°C). Excessively cold temperatures (<-10°C) should be avoided; studies have shown greater losses of analytes due to reduced pressures in the container, sublimation of water, and concomitant release of water-soluble VOCs into the headspace. Upon opening the container, the vacuum is quickly replaced with ambient air, thus purging out VOCs from the headspace (Maskarinec et al., 1988). Extremely cold temperatures can also loosen the seal on the container cap. Caps should be retightened after 15 minutes at reduced temperatures. Samples should be kept in ice chests while in route to the shipment facility or laboratory. At temperatures above freezing, bacterial action can have a significant impact on the observed soil VOC concentration. Numerous preservation techniques are being evaluated at the University of Nevada Environmental Research Center in Las Vegas and at Oak Ridge National Laboratory.

SHIPPING

Given the short holding times required for VOC analysis under Method 8240 (10 days from sample collection to analysis), samples are usually shipped via air carrier to the analytical laboratory. Samples should be well packed and padded to prevent breakage. Temperatures in cargo holds can increase to more than 50°C during transit, therefore, the need for adequate cold storage is critical. Styrofoam coolers are commercially available to accommodate 40-mL and 125-mL glass containers. Sufficient quantities of Blue Ice™ or Freeze-Gel™ packs should be placed in the container to ensure that samples are cooled for the duration of the shipment. A maximum-minimum thermometer (non-mercury) should be shipped with the samples. If sample containers are not adequately sealed, VOC losses can occur. These losses may be exacerbated by the reduced atmospheric pressures encountered in the cargo holds of air carriers. Figure 6 illustrates the changes in temperature and pressure in the cargo hold of various air carrier's aircraft. Three major air carriers have been monitored and have shown similar fluctuations in temperature and pressure (Lewis and Parolini, 1991). Lewis et al. (1990) noted decreases in VOC concentrations in soil samples that were shipped compared to samples that were analyzed in the field. If the container is of questionable or unknown integrity, it should either be evaluated prior to use or a previously characterized container should be used.

As discussed previously, samples that are immersed in methanol have special shipping requirements. These samples must be shipped as "Flammable Liquids" under Department of Transportation (DOT) requirements. A secondary container is required for shipment of any item classified as a flammable liquid.

PRESERVATION

Improvements in operational factors such as sampling device efficiency, sample transfer, containerizing, shipping, storage, laboratory sample preparation, and analysis will reduce VOC losses from soils. Two principal matrix-specific factors that can contribute to the loss of VOC in soils are biodegradation and volatilization. An effective preservation technique should act on these matrix-specific factors to reduce losses of VOCs.

The required preservation technique for soil samples is storage at 0° to 4°C in the dark. This technique retards biodegradation

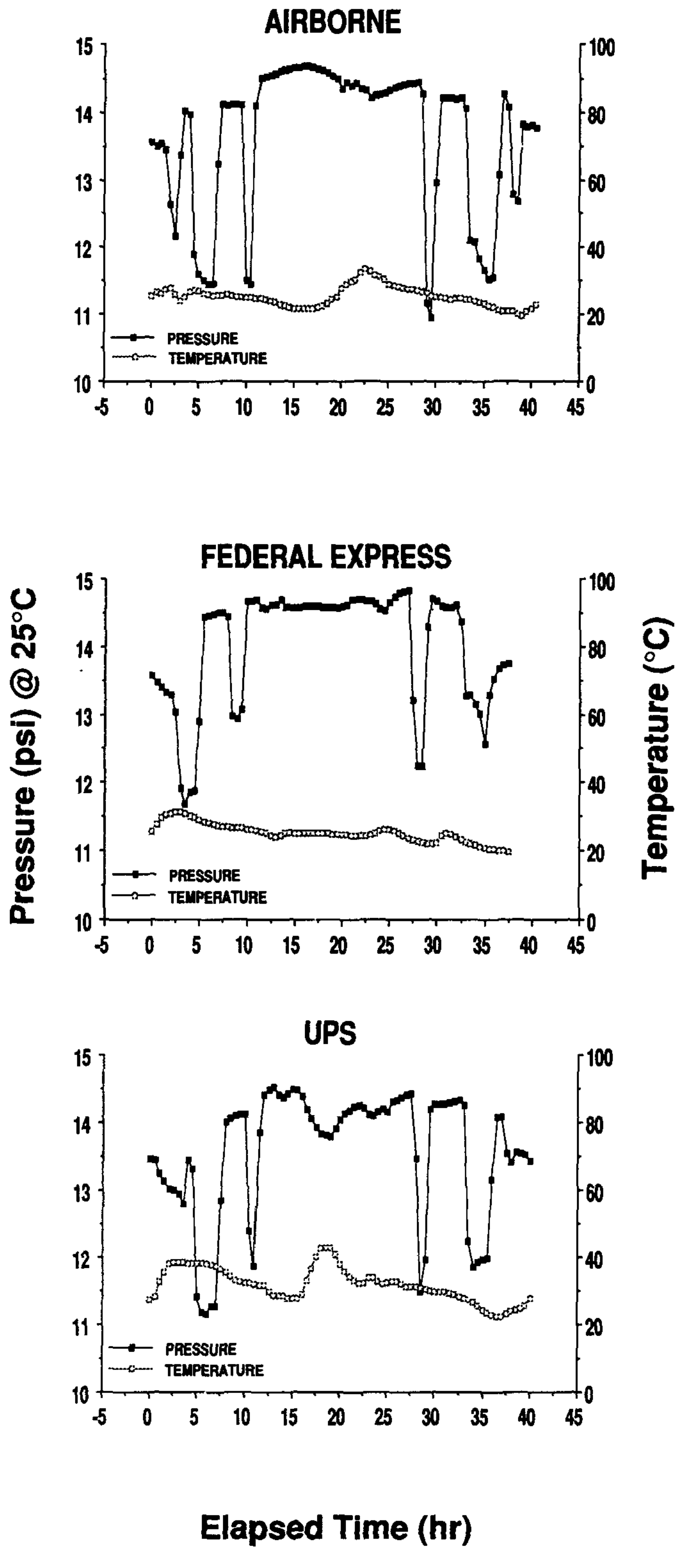

Figure 6. Temperature and pressure fluctuations recorded in the cargo hold of various air carriers. Recording device was shipped from Las Vegas, NV, to Pearl River, NY, and returned.

processes mediated by soil microorganisms. Some microorganisms, however, such as fungi, are biologically active even at 4°C. Wolf et al. (1989) investigated several methods (i.e., chemical and irradiation) for sterilizing soil and concluded that mercuric chloride is one of the most effective preservatives that causes minimal changes to the chemical and physical properties of the soil. Stuart et al. (1990) utilized mercuric chloride as an antimicrobial preservative to stabilize ground-water samples contaminated with gasoline. Other researchers (U.S. EPA 1991a) have used mercuric chloride to retard biodegradation of VOCs in soil samples. The soils were spiked with 150 µg/kg of Target Compound List (TCL) VOCs and were preserved with 2.5 mg of mercuric chloride per 5 g of soil. The results indicated that the amount of mercuric chloride needed to reduce biodegradation was directly related to the soil's organic carbon content. In addition, the levels of mercuric chloride added to samples did not interfere with sample handling or analysis. Currently, research is underway to quantitate the required mercuric chloride concentration as a function of soil organic content.

The loss of VOCs through volatilization is reduced by optimizing sample handling procedures. When samples require laboratory pretreatment, severe losses of VOCs (up to 100%) have been observed. In order to minimize volatilization losses, several preservatives have been examined (U.S. EPA 1991a), including solid adsorbents, anhydrous salts, and water/methanol extraction mixtures. The most efficient preservatives for reducing volatilization of VOCs from soils have been two solid adsorbents, Molecular Sieve - 5A™ (aluminum silicate desiccant) and Florasil™ (magnesium silicate desiccant). The addition of 0.2 mg per 5 g of soil greatly increased the recovery of VOCs from spiked samples. The mechanism is believed to involve the displacement of water from adsorption sites on the soil particle and binding of VOCs to these freed sites. Currently, research is in progress with soils obtained from actual contaminated sites.

LABORATORY PROCEDURES

Sample Storage

Most regulatory procedures specify storage of samples for VOA at 4°C in the dark. Sample coolers should be opened under chain-of-custody conditions, and the temperature inside the cooler should be verified and noted. Samples should be transferred to controlled-temperature (4°C) refrigerators until analysis. In many cases, insufficient cooling is provided during transport. In these cases, data quality may be compromised.

Sample Preparation

The two most commonly used methods that satisfy regulatory requirements for the analysis of soil samples for VOCs are direct purge and trap and methanol extraction. Each procedure has benefits and limitations with respect to sample preparation prior to VOC analysis of soils.

The modified purge-and-trap procedure has the following characteristics:

- Homogenization of contents of wide-mouth jar will cause significant VOC losses. The collection of a 5-g aliquot in the field and placement into a tared vial sealed with a modified purge-and-trap cap is recommended.
- Surrogate addition should be made to the soil in the field, if possible.
- May be more susceptible to short-range spatial variability.
- Samples should be brought to ambient temperature before purging.
- May be more suitable for low-level samples.

The methanol-immersion procedure has the following characteristics:

- The key is to minimize the time samples are exposed to the atmosphere prior to immersion into methanol.
- Minimum detection limits can be raised by a factor of 10 to 20.
- The best option for sample archival because VOCs are highly soluble in methanol.
- Large-mass samples can be extracted in the field in a 1:1 ratio and the methanol extract shipped to the laboratory for analysis.
- Can collect composite samples.

The analytical methods that can be used for the analysis of soils for VOCs are summarized in Table 12. An analytical method should be selected that is compatible with the recommended sample collection and containerizing procedure discussed earlier.

CONCLUSIONS AND RECOMMENDATIONS

Current research on sampling soils for VOC analyses answers many of the questions asked by RPMs and OSCs who conduct site characterization and restoration.

1. There is no specific method or process that can be recommended for sampling soils for VOA. A wide variety of sampling devices are currently used for collecting soil samples for VOA. Sampling device selection is site-specific, and no single device can be recommended for use at all sites. Several different samplers, which cover a broad range of sampling conditions and circumstances, are recommended for obtaining representative samples for VOC analysis (Table 7). Procedures may vary for different VOCs. Experiments have shown that a procedure that collects an undisturbed, intact sample with a device that allows direct transfer to a sample container (e.g., split-spoon, Shelby tube, or zero-contamination sampler) is superior to a more disruptive procedure that uses a crude bulk sampler (e.g., shovel, trowel, scoop, or spade) for maintaining the integrity of VOCs in a soil sample. Large-diameter tube-type sampling devices are recommended for collection of near-surface samples. The same types of devices can be used in conjunction with hollow-stem augers for collecting subsurface samples.
2. Transfer of the sample from the sampling device to the container is a critical step in the process. Losses of as much as 80% have been observed during this step. The faster the soil can be removed from the sampling device and

TABLE 12. METHODS FOR VOC ANALYSIS OF SOIL

Method Extraction/analysis	Sample Size (g)	Sample Preparation Procedure	Sensitivity (μg/kg)	Data Quality Objective	Program	Comments
5030 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5	Purge and trap	5-10	Litigation	RCRA[a]	Sample transfer to purge and trap is critical.
5380 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5-100	Methanol extraction	500-1000	Litigation	RCRA	Sensitivity loss but sample transfer facilitated.
5031 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5	Field purge	5-10	Semi-quantitative	RCRA	Sample can only be analyzed once, transfer and shipping facilitated.
3810 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	10	Heat to 90°C in water bath and analyze headspace	1000	Screening for purgeable organics	RCRA	Can be performed in the field.
3820	10	Hexadecane extraction followed by GC/FID	500-1000	Screening prior to GC or GC/MS analysis	RCRA	FID responses vary with type of VOC.
624	5	Purge and trap	5-10	Litigation	CLP[b]	Similar to method 5030/8240 in RCRA SW-846.

[a] U.S. EPA, 1986b
[b] U.S. EPA, 1982

transferred into an airtight sample container, the smaller the VOC loss. Liners make the removal and subsampling of soil from the collection device more efficient.

3. The best method for transferring a sample from a large-diameter coring device (or exposed test pit) into a sample container is by collecting the appropriate size aliquot (for laboratory analysis) with a small-diameter, hand-held corer and extruding the subsample into a 40-mL VOA vial, then sealing the vial with a modified purge-and-trap cap. Alternatively, contents of the large-diameter coring device can be sectioned and immersed in methanol.

4. Small-diameter, hand-held corers can be used for collecting samples from a freshly exposed face of a trench or test pit, or for obtaining a subsample from a large-diameter coring device. The use of a small-diameter, hand-held corer is recommended for obtaining subsamples from liner-held soil. Collection of a sample of the appropriate size for a particular analytical procedure is optimal. The required size of aliquot can be extruded into a 40-mL VOA vial and sealed with a modified purge-and-trap cap. The possibility exists of compositing several small-diameter core samples by immersing them in a single jar containing methanol.

5. Sample containers vary in terms of air-tightness. Data are available to indicate that there is a decrease in pressure and an increase in temperature in the cargo holds of certain air carriers. This is the worst possible set of conditions for maintaining VOCs in containerized soil samples. Intact seals on storage containers and adequate cooling is thus critical for maintaining VOCs in soil samples. Shipping and holding-time studies have shown that vials and jars may be equally suited for containing VOCs in soil samples, the laboratory pretreatment step needed to obtain an aliquot from a jar-held sample causes significant losses of VOCs. Commercially available shipping packages with built-in cooling materials (e.g., Freeze Gel Packs® or Blue Ice®) are available. Whenever possible, an integrated sampling approach should be employed to obtain the most representative samples possible. Soil-gas surveying coupled with on-site soil sampling and analyses followed by the Resource Conservation and Recovery Act (RCRA) or CLP laboratory analyses may provide valuable information on the partitioning of VOCs at a site.

6. The current preservation technique for soil samples is storage at 4°C in the dark. Biological activity may continue at this temperature. The addition of mercuric chloride to the soil may reduce biodegradation of VOCs. The amount of mercuric chloride to be added, however, is a function of the organic carbon content in the soil. The most promising preservatives for reducing losses of VOCs through volatilization are solid adsorbents such as Molecular Sieve - 5A™ and Florasil™.

REFERENCES CITED

49 CFR, 1982. Code of Federal Regulations, 49, Parts 100 to 177, October 1, 1982, pp. 231.

Acker, W. L. 1974. Basic Procedures for Soil Sampling and Core Drilling. Acker Drill Co., Inc., Scranton, PA, 246 pp.

Arneth, J.-D., G. Milde, H. Kerndorff, and R. Schleyer. 1988. Waste deposit influences on groundwater quality as a tool for waste type and site selection for final storage quality. In: P. Baccini (Ed.) The Landfill: Reactor and Final Storage, Swiss Workshop on Land Disposal of Solid Wastes, Gerzensee, March, 14-17, pp. 399-415.

Barcelona, M. J. 1989. Overview of the Sampling Process. In: Keith, L. H. (Ed.), Principles of Environmental Sampling, American Chemical Society, Washington, D.C., pp. 3-23.

Barth, D. S., B. J. Mason, T. H. Starks, and K. W. Brown. 1989. Soil Sampling Quality Assurance User's Guide (2nd edition), EPA 600/8-89/046, U.S. EPA, EMSL-LV, Las Vegas, NV, March, 225 pp.

Boucher, F. R. and G. F. Lee. 1972. Adsorption of Lindane and *Dieldrin pesticides on unconsolidated aquifer sands*. Env. Sci. Tech. 6:538-543.

Bouwer, E. J. 1984. Biotransformation of organic micropollutants in the subsurface. In: Petroleum Hydrocarbons and Organic Chemicals in Ground Water. National Well Water Association, Dublin, OH.

Cameron, R. E. 1963. Algae of southern Arizona - Part 1. Introduction to blue-green algae. Rev. Alg. N.S. 6(4):282-318.

Chiou, C. T. and T. D. Shoup. 1985. Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. Env. Sci. Tech. 19(12):1196-1200.

Chiou, C. T., D. E. Kile, and R. L. Malcolm. 1988. Sorption of vapors of some organic liquids on soil humic acid and its relation to partitioning of organic compounds in soil organic matter. Env. Sci. Tech. 22(3):298-303.

Dean, J. D., P. S. Huyakorn, A. S. Donigan, Jr., K. A. Voos, R. W. Schanz, Y. J. Meeks, and R. F. Carsel. 1989. Risk of Unsaturated/Saturated Transport and Transformation of Chemical Concentrations (RUSTIC) - Volume I: Theory and Code Verification, EPA/600/3-89/048a, Environmental Research Laboratory, U.S. EPA, Athens, GA, 203 pp.

Devitt, D. A., R. B. Evans, W. A. Jury, T. H. Starks, B. Eklunk, and A. Gholson. 1987. Soil Gas Screening for Detection and Mapping of Volatile Organics. National Well Water Association, Dublin, OH, 270 pp.

Farmer, W. J., M.-S. Yang, J. Letey, and W. S. Spencer. 1980. Land Disposal of Hexachlorobenzene Wastes: Controlling Vapor Movement in Soils. EPA-600/2-80-119, U.S. EPA, Environmental Research Laboratory, Cincinnati, OH, August 1980.

Gillman, R. W. and S.F. O'Hannesin. 1990. Sorption of aromatic hydrocarbons by materials used in construction of ground-water sampling wells. In: D. M. Nielsen and A. I. Johnson (eds.), *Ground Water and Vadose Zone Monitoring*, ASTM STP 1053, American Society of Testing Materials, Philadelphia, PA, pp. 108-122.

Hanisch, R. C. and M. A. McDevitt. 1984. Protocols for Sampling and Analysis of Surface Impoundments and Land Treatment/ Disposal Sites for VOCs. Technical Note. EPA-EMB 68-02-3850, Work Assignment 11.

Jamison, V. W., R. L. Raymond, and J. O. Hudson. 1975. Biodegradation of high-octane gasoline. In: Proceedings of the Third International Biodegradation Symposium. Applied Science Publishers Ltd., London.

Johnson, R. E. 1976. Degradation of DDT by Fungi. ResiDue Review 61:1-28.

Jury, W. A. 1984. A User's Manual for the Environmental Fate Screening Model Programs BAM and BCM, Dept. Soil and Environ. Sci., Univ. of California, Riverside, CA. Submitted to the California Department of Health Services.

Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

Kleopfer, R. D. et al. 1985. Anaerobic degradation of trichloroethylene in soil. Env. Sci. Tech. 19:277-284.

Kobayashi, H. and B. E. Rittman. 1982. Microbial removal of hazardous organic compounds. Env. Sci. Tech. 16(3):170A-183A.

Lechevalier, H. A. and M. P. Lechevalier. 1976. Actinomycetes found in sewage treatment plants of the activated sludge type. In: Actinomycetes: The Boundry Microorganisms, Toppen Co., Ltd., Tokyo, Japan.

Lewis, T. E., B. A. Deason, C. L. Gerlach, and D. W. Bottrell. 1990. Performance evaluation materials for the analysis of volatile organic compounds in soil: A preliminary assessment. J. Env. Sci. Health A25(5):505-531.

Lewis, T. E. and J. R. Parolini. 1991. Temperature and pressure fluctuations in air shipped samples: Implications on sample integrity. Analyst (in preparation).

Lotse, E. G., D. A. Graetz, G. Chesters, G. B. Lee, and L. W. Newland. 1968. Lindane adsorption by lake sediments. Env. Sci. Tech. 2:353-357.

Maskarinec M. P., 1990 Personal Communication.

Maskarinec, M. P., L. H. Johnson, S. K. Holladay. 1988. Preanalytical holding times. Paper presented at the Quality Assurance in Environmental Measurements Meeting, U.S. Army Toxic and Hazardous Materials Agency, Baltimore, MD, May 25-26, 1988.

McCoy, D. E. 1985. "301" studies provide insight into future of CERCLA. The Hazardous Waste Consultant 3/2:18-24.

Plumb, R. H., Jr. 1987. A practical alternative to the RCRA organic indicator parameters. In: T. Bursztynsky (Ed.) Proceedings of Hazmacon 87, Santa Clara, CA, April 21-23, pp. 135-150.

Plumb, R. H., Jr., and A. M. Pitchford. 1985. Volatile organic scans: Implications for ground water monitoring. Paper presented at the National Water Well Association/American Petroleum Institute Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, TX, November 13-15, 1985.

Richardson, E. M. and E. Epstein. 1971. Retention of three insecticides on different size soil particles suspended in water. Soil Sci. Soc. Am. Proc. 35:884-887.

Roy, W. R. and R. A. Griffin. 1985. Mobility of organic solvents in water-saturated soil materials, Environ. Geol. Wat. Sci. 7(4):241-247.

Shen, T. T. and G. H. Sewell. 1982. Air pollution problems of uncontrolled hazardous waste sites. In: Proceedings of 1982 Superfund Conference, Hazardous Materials Control Research Institute, Washington, pp. 76-80.

Siegrist, R. L. 1990. Volatile organic compound measurements in contaminated soils: The state of practice, methods development, and implications for remediation projects. J. Haz. Mat. (in press).

Siegrist, R. L. and P. D. Jennsen. 1990. Evaluation of sampling method effects on volatile organic compound measurements in contaminated soils. Env. Sci. Tech. 24:1387-1392.

Smith, J. A., C. T. Chiou, J. A. Kammer, and D. E. Kile. 1990. Effect of soil moisture on the sorption of trichloroethene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. Env. Sci. Tech. 24:676-683.

Spencer, W. F. and M. M. Cliath. 1970. Soil Sci. Soc. Am. Proc. 34:574-579.

Spencer, W. F., M. M. Cliath, W. A. Jury, and L.-Z. Zhang. 1988. Volatilization of organic chemicals from soil as related to their Henry's Law constants. J. Env. Qual. 17(3):504-509.

Stuart, J. D., V. D. Roe, W. M. Nash, and G. A. Robbins. 1990. Manual headspace method to analyze for gasoline contamination of ground water by capillary column gas chromatography. Personal Communication.

U.S. EPA. 1982. Test Method 624 (Purgeables). Methods for Organic Chemical Analysis of Municipal and Industrial Wastes, EPA-600/4-82-057, U.S. EPA Environmental Support Laboratory, Cincinnati, OH.

U.S. EPA. 1983. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II - Available Sampling Methods. EPA-600/4-83-040.

U.S. EPA. 1986a. Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units, EPA/530/-SW-86-040, pp 11-62.

U.S. EPA. 1986b. Test Methods for Evaluating Solid Waste (SW-846), Method 8240, Off. Solid Waste and Emergency Response (3rd Edition).

U.S. EPA. 1987. Data Quality Objectives for Remedial Response Activities: Development Process. EPA/540/G-87/003, Off. Solid Waste and Emergency Response, Washington, D.C.

U.S. EPA. 1988. Field Screening Method Catalog User's Guide. EPA/540/2-88/005, Sept. 1988, Office of Emergency and Remedial Response, Washington, D.C.

U.S. EPA. 1991a. Investigation of Sample and Sample Handling Techniques for the Measurement of Volatile Organic Compounds in Soil. University of Nevada, Las Vegas, submitted to U.S. EPA, Environmental Monitoring Systems Laboratory, Las Vegas, NV (in preparation).

U.S. EPA. 1991b. Manual for Sampling Soils for Volatile Organic Compounds. Environmental Monitoring Systems Laboratory, Las Vegas, NV, 26 pp. (in preparation).

van Ee, J. J., L. J. Blume, and T. H. Starks. 1990. A Rationale for the Assessment of Errors in the Sampling of Soils, EPA/600/4-90/013, Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV, 57 pp.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, New York, NY (2nd Edition).

Vogel, T. M. and P. L. McCarty. 1985. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. Appl. Environ. Microbiol. 49:1080-1084.

Voice, T. C. and W. J. Weber, Jr. 1983. Sorption of hydrophobic compounds by sediments, soils, and suspended solids - I. Theory and background. Wat. Res. 17(10):1433-1441.

Wolf, D. C., T. H. Dao, H. D. Scott, and T. L. Lavy. 1989. Influence of sterilization methods on selected soil microbiological, physical, and chemical properties. J. Env. Qual. 18:39-44.

☆U.S. GOVERNMENT PRINTING OFFICE: 1991 - 548-187/25633

Environmental Protection
Agency

Information
Cincinnati OH 45268-1072

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35

Official Business
Penalty for Private Use, $300

Please make all necessary changes on the above label, detach or copy, and return to the address in the upper left-hand corner

If you do not wish to receive these reports CHECK HERE □, detach, or copy this cover, and return to the address in the upper left-hand corner

EPA/540/4-91/001

United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/4-91/001 February 1991

EPA

Ground-Water Issue

SOIL SAMPLING AND ANALYSIS FOR VOLATILE ORGANIC COMPOUNDS

T. E. Lewis, A. B. Crockett, R. L. Siegrist, and K. Zarrabi

The Regional Superfund Ground Water Forum is a group of ground-water scientists that represents EPA's Regional Superfund Offices. The forum was organized to exchange up-to-date information related to ground-water remediation at Superfund sites. Sampling of soils for volatile organic compounds (VOCs) is an issue identified by the Ground Water Forum as a concern of Superfund decision makers.

A group of scientists actively engaged in method development research on soil sampling and analysis for VOCs gathered at the Environmental Monitoring Systems Laboratory in Las Vegas to examine this issue. Members of the committee were R. E. Cameron (LESC), A. B. Crockett (EG&G), C. L. Gerlach (LESC), T. E. Lewis (LESC), M. P. Maskarinec (ORNL), B. J. Mason (ERC), C. L. Mayer (LESC), C. Ramsey (NEIC), S. R. Schroedl (LESC), R. L. Siegrist (ORNL), C. G. Urchin (Rutgers University), L. G. Wilson (University of Arizona), and K. Zarrabi (ERC). This paper was prepared by The Committee for EMSL-LV's Monitoring and Site Characterization Technical Support Center, under the direction of T. E. Lewis, with the support of the Superfund Technical Support Project. For further information contact Ken Brown, Center Director at EMSL-LV, FTS 545-2270, or T. E. Lewis at (702) 734-3400.

PURPOSE AND SCOPE

Concerns over data quality have raised many questions related to sampling soils for VOCs. This paper was prepared in response to some of these questions and concerns expressed by Remedial Project Managers (RPMs) and On-Scene Coordinators (OSCs). The following questions are frequently asked:

1. Is there a specific device suggested for sampling soils for VOCs?
2. Are there significant losses of VOCs when transferring a soil sample from a sampling device (e.g., split spoon) into the sample container?
3. What is the best method for getting the sample from the split spoon (or other device) into the sample container?
4. Are there smaller devices such as subcore samplers available for collecting aliquots from the larger core and efficiently transferring the sample into the sample container?
5. Are certain containers better than others for shipping and storing soil samples for VOC analysis?
6. Are there any reliable preservation procedures for reducing VOC losses from soil samples and for extending holding times?

This paper is intended to familiarize RPMs, OSCs, and field personnel with the current state of the science and the current thinking concerning sampling soils for VOC analysis. Guidance is provided for selecting the most effective sampling device for collecting

Communication • Training • Technology Support — Technology Support Project

Superfund Technology Support Center for Monitoring and Site Characterization

Environmental Monitoring Systems Laboratory Las Vegas, NV

Technology Innovation Office
Office of Solid Waste and Emergency Response,
U.S. EPA, Washington, D.C.

Walter W. Kovalick, Jr., Ph.D., Director

Printed on Recycled Paper

samples from soil matrices. The techniques for sample collection, sample handling, containerizing, shipment, and storage described in this paper reduce VOC losses and generally provide more representative samples for volatile organic analyses (VOA) than techniques in current use. For a discussion on the proper use of sampling equipment the reader should refer to other sources (Acker, 1974; U.S. EPA, 1983; U.S. EPA, 1986a).

Soil, as referred to in this report, encompasses the mass (surface and subsurface) of unconsolidated mantle of weathered rock and loose material lying above solid rock. Further, a distinction must be made as to what fraction of the unconsolidated material is soil and what fraction is not. The soil component here is defined as all mineral and naturally occurring organic material that is 2 mm or less in size. This is the size normally used to differentiate between soils (consisting of sands, silts, and clays) and gravels.

Although numerous sampling situations may be encountered, this paper focuses on three broad categories of sites that might be sampled for VOCs:

1. Open test pit or trench
2. Surface soils (< 5 ft in depth)
3. Subsurface soils (> 5 ft in depth)

INTRODUCTION

VOCs are the class of compounds most commonly encountered at Superfund and other hazardous waste sites (McCoy, 1985; Plumb and Pitchford, 1985; Plumb, 1987; Arneth et al., 1988). Table 1 ranks the compounds most commonly encountered at Superfund sites. Many VOCs are considered hazardous because they are mutagenic, carcinogenic, or teratogenic, and they are commonly the controlling contaminants in site restoration projects. Decisions regarding the extent of contamination and the degree of cleanup have far-reaching effects; therefore, it is essential that they be based on accurate measurements of the VOC concentrations present. VOCs, however, present sampling, sample handling, and analytical difficulties, especially when encountered in soils and other solid matrices.

Methods used for sampling soils for volatile organic analysis (VOA) vary widely within and between EPA Regions, and the recovery of VOCs from soils has been highly variable. The source of variation in analyte recovery may be associated with any single step in the process or all steps, including sample collection, transfer from the sampling device to the sample container, sample shipment, sample preparation for analysis, and sample analysis. The strength of the sampling chain is only as strong as its weakest link; soil sampling and transfer to the container are often the weakest links.

Sample collection and handling activities have large sources of random and systematic errors compared to the analysis itself (Barcelona, 1989). Negative bias (i.e., measured value less than true value) is perhaps the most significant and most difficult to delineate and control. This error is caused primarily by loss through volatilization during soil sample collection, storage, and handling.

TABLE 1. RANKING OF GROUND WATER CONTAMINANTS BASED ON FREQUENCY OF DETECTION AT 358 HAZARDOUS WASTE DISPOSAL SITES

Contaminant	Detection Frequency
Trichloroethene (V)	51.3
Tetrachloroethene (V)	36.0
1,2-trans Dichloroethene (V)	29.1
Chloroform (V)	28.4
1,1-Dichloroethene (V)	25.2
Methylene chloride (V)	19.2
1,1,1-Trichloroethane (V)	18.9
1,1-Dichloroethane (V)	17.9
1,2-Dichloroethane (V)	14.2
Phenol (A)	13.6
Acetone (V)	12.4
Toluene (V)	11.6
bis-(2-Ethylhexyl) phthalate (B)	11.5
Benzene (V)	11.2
Vinyl chloride	8.7

V = volatile, A = acid extractable, B = base/neutral
Source: Plumb and Pitchford (1985).

There are currently no standard procedures for sampling soils for VOC analyses. Several types of samplers are available for collecting intact (undisturbed) samples and bulk (disturbed) samples. The selection of a particular device is site-specific. Samples are usually removed from the sampler and are placed in glass jars or vials that are then sealed with Teflon-lined caps. Practical experience and recent field and laboratory research, however, suggest that procedures such as these may lead to significant VOC losses (losses that would affect the utility of the data). Hanisch and McDevitt (1984) reported that any headspace present in the sample container will lead to desorption of VOCs from the soil particles into the headspace and will cause loss of VOCs upon opening of the container. Siegrist and Jennsen (1990) found that 81% of the VOCs were lost from samples containerized in glass jars sealed with Teflon-lined caps compared to samples immersed in methanol in jars.

FACTORS AFFECTING VOC RETENTION AND CONCENTRATION IN SOIL SYSTEMS

Volatile organic compounds in soil may coexist in three phases: gaseous, liquid (dissolved), and solid (sorbed). [Note: "Sorbed" is used throughout this paper to encompass physical and chemical adsorption and phase partitioning.] The sampling, identification, and quantitation of VOCs in soil matrices are complicated because VOC molecules can coexist in these

United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/4-90/053 October 1990

EPA Ground Water Issue

Basic Concepts of Contaminant Sorption at Hazardous Waste Sites

Marvin D. Piwoni* and Jack W. Keeley**

Introduction

The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA's Regional Superfund Offices, organized to exchange up-to-date information related to ground-water remediation of Superfund sites. One of the major issues of concern to the Forum is the transport and fate of contaminants in soil and ground water as related to subsurface remediation. Processes which influence the behavior of contaminants in the subsurface must be considered both in evaluating the potential for movement as well as in designing remediation activities at hazardous waste sites. Such factors not only tend to regulate the mobility of contaminants, but also their form and stability. Sorption is often the paramount process controlling the behavior of contaminants in the subsurface. This paper summarizes the basic concepts of sorption in soil and ground water with emphasis on nonpolar organic contaminants.

For further information contact: Joe Williams, FTS 743-2246; Bert Bledsoe, 743-2324; or Dom DiGiulio, 743-2271 at RSKERL-Ada.

The Concept of Sorption

Sorption can be defined as the interaction of a contaminant with a solid. More specifically, the term can be further divided into adsorption and absorption. The former refers to an excess contaminant concentration at the surface of a solid while the latter implies a more or less uniform penetration of the solid by a contaminant. In most environmental settings this distinction serves little purpose as there is seldom information concerning the specific nature of the interaction. The term sorption is used in a generic way to encompass both phenomena.

There are a number of factors which control the interaction of a contaminant and the surface of soil or aquifer materials. These include chemical and physical characteristics of the contaminant, composition of the surface of the solid, and the fluid media encompassing both. By gaining an understanding of these factors, logical conclusions can often be drawn about the impact of sorption on the movement and distribution of contaminants in the subsurface. The failure to take sorption into account can result in a significant underestimation of the amount of a contaminant at a site as well as the time required for it to move from one point to another.

In introducing sorption theory it is necessary to define the terms sorbate and sorbent. The sorbate is the contaminant that adheres to the sorbent, or sorbing material. In this discussion the sorbate will usually be an organic molecule and the sorbent will be the soil or aquifer matrix.

This Issue Paper is condensed from a presentation given at the EPA/EPRI Workshop on Leachate Testing Methods in Houston, Texas, in January 1989.

Factors Influencing Sorption

The properties of a contaminant have a profound impact on its sorption behavior. Some of these include:

- Water Solubility
- Polar/Ionic Character
- Octanol/Water Partition Coefficient
- Acid/Base Chemistry
- Oxidation/Reduction Chemistry

* *Laboratory Services Manager, Hazardous Waste Research and Information Center, Illinois Department of Energy and Natural Resources.*

** *Environmental Engineer, Dynamac Corporation, Robert S. Kerr Environmental Research Laboratory.*

COMMUNICATION · TRAINING · TECHNOLOGY SUPPORT
Technical Support Project

Superfund Technology Support Center for Ground Water

Robert S. Kerr Environmental Research Laboratory
Ada, OK

Printed on Recycled Paper

Contaminant Characteristics

In discussing sorption it is useful to divide chemicals into three groups. Although there are many ways to divide chemicals into subgroups, for this purpose three categories are presented which transcend normal boundaries between inorganic and organic species. These are: (1) ionic or charged species; (2) uncharged polar species; and, (3) uncharged nonpolar species.

Most inorganic chemicals in aqueous solution will occur as ionic or charged species. This applies to metals and metalloids, and to other molecules such as cyanide and ammonia. However, in contaminated water, metals and other inorganic constituents can exist as polar or nonpolar neutral species. In any event, the chemical form of a contaminant will have a profound effect on its sorption and, therefore, its environmental mobility.

Organic contaminants have representatives in all three of the sorption categories. Many of the more common organic groundwater contaminants are of the nonpolar species, including trichloroethene (TCE), tetrachloroethene (PCE), the chlorinated benzenes, and the more soluble components of hydrocarbon fuels such as benzene, toluene and xylene. Other important organic contaminants including many of the pesticides, phenols and dyes exist in solution as either charged or polar molecules.

Still other, larger organics, such as surfactants, can have both polar and nonpolar ends within the same molecule. The environmental mobility of contaminants with these distinctive properties has been less thoroughly studied than nonpolar organics; therefore, site-specific investigations may provide the most reliable information for their transport characteristics.

Soil Characteristics

If one avoids the difference between positive and negative charges, a simple rule of sorption might be: for charged species, "opposites attract" and for uncharged species, "likes interact with likes." Likes refers to the three categories of contaminants and to the properties of the soil matrix. Some of the most important characteristics of soil affecting the sorptive behavior of subsurface materials include:

- Mineralogy
- Permeability/Porosity
- Texture
- Homogeneity
- Organic Carbon Content
- Surface Charge
- Surface Area

Soil, in its natural state, is primarily composed of sand, silt, clay, water, and a highly variable amount of natural organic carbon. The latter profoundly complicates a soil's sorptive properties. The combination of these characteristics describes the surfaces offered as sorptive sites to contaminants in water passing through the subsurface matrix. For example, silts and clays have much higher surface areas than sand, usually carry a negative charge, and almost invariably associate with natural organic matter.

It can be deduced that sandy materials offer little in the way of sorptive surfaces to passing contaminants while silts and clays, particularly those having substantial amounts of organic matter, provide a rich sorptive environment for all three categories of contaminants. Even the most porous and highly productive aquifers, composed of sands and gravels, usually have some fine grained material, and a few percent of silts and clays can result in a substantial increase in the sorptive behavior of the aquifer material.

Fluid Media Characteristics

Under most contamination situations the primary transporting fluid is water. One of the most important properties of this solvent phase is pH for it dictates the chemical form and, therefore, the mobility, of all contaminants susceptible to the gain or loss of a proton. As an example, pentachlorophenol will primarily be an uncharged polar molecule in an aqueous solution whose pH is below about 4.7 and an anion when the pH is above that value, increasing its solubility from 14 to 90 mg/l.

Other characteristics of water that can influence the behavior of contaminants include the salt content and the dissolved organic carbon content. Chlorides, for example, which are not usually of much concern when dealing with organic contaminants, can have an important effect on the mobility of various metals. Dissolved organic matter, at relatively high concentrations found in many leachates, has a significant effect on the mobility of most nonpolar organics.

Implications of These Characteristics

Although somewhat simplified, it can be assumed for purposes of this discussion, that charged and polar species tend to interact with charged and polar surfaces, and nonpolar compounds interact with nonpolar components of soil, usually the natural organic carbon. In order to make a first estimate of the significance of sorption at a site, it is necessary to determine the polar and nonpolar nature of the material with which the contaminant will come into contact. This is usually done by measuring the cation exchange capacity and the natural organic carbon content, respectively.

The cation exchange capacity (CEC) provides an estimate of the total negatively-charged sites on the surface of the soil. It is determined by measuring the mass of a standard cation, usually ammonia, that displaces another cation held by the soil. Under normal field conditions these sites will be occupied by cations common to the flowing or percolating water, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. Larger organic cations and highly-charged metal ions like Hg^{2+} or Cr^{3+} will be preferentially retained at these sites by "exchanging" with their normal occupants. Thus large organic cations and heavy metals would not normally be expected to move far through soils with a measurable cation exchange capacity.

At contaminated sites, however, conditions may not be "normal" and Hg^{2+} may be codisposed with high levels of chloride salts. In the complexation chemistry shown in Figure 1, Hg^{2+} may be replaced by the neutral complex $HgCl_2$ or the negative ion $HgCl_3$, both of which move through the soil more quickly than the cationic form.

Sorption of Nonpolar Organics

As mentioned above the chemicals at many contaminated sites are nonpolar organics. It was representatives of these types of compounds (DDT and other chlorinated hydrocarbon pesticides) that first focused attention on the potential hazards of chemicals in the environment because of their widespread use, potential human toxicity, and recalcitrance.

$$Hg^{2+} + Cl^- \longleftrightarrow HgCl^+$$

$$HgCl^+ + Cl^- \longleftrightarrow HgCl_2^0$$

$$HgCl_2^0 + Cl^- \longleftrightarrow HgCl_3^-$$

$$HgCl_3^- + Cl^- \longleftrightarrow HgCl_4^{2-}$$

The complexation reactions are driven right and down by increasing chloride concentrations, often characteristic of waste waters. Increased complexation produces increased environmental mobility of the mercury.

Figure 1. Mercury Ion Complexation in Chloride-Rich Water

Transport and fate characteristics of these compounds have been well studied, first by the agricultural community and later by environmental scientists. As a result, an understanding of the sorptive behavior of these compounds has evolved which can be used to assess the environmental consequences posed at a waste disposal site.

Many organics of environmental concern have a limited solubility in water because of their nonpolarity and molecular size: that is, the solubility of an organic contaminant decreases with decreasing polarity and increasing molecular size. But even with limited solubilities, many hazardous chemicals at equilibrium are at measurable, and sometimes toxic concentrations in water. Polar molecules, such as ethanol, are compatible with water. Their combination results in a homogeneous solution regardless of the proportions that are mixed.

Nonpolar organic compounds interact with soil organic matter through a process known as "hydrophobic sorption" which can be explained as the affinity of organic compounds for phases other than water. For example, water being a polar molecule is not compatible with other nonpolar molecules, such as DDT, which is immiscible with water.

Octanol-Water Partitioning

Organic molecules of increasing size, decreasing polarity and therefore water solubility, are said to exhibit increasing "hydrophobicity" which can be quantified by their octanol-water partition coefficient. It is a measure of the distribution of the chemical between a water and an organic (octanol) phase with which it is in contact. The more hydrophobic the contaminant, the more likely it is to partition into the octanol phase. The partition coefficient provides a fairly accurate understanding of the sorptive process occurring between water and the soil, more specifically, the soil organic matter.

The octanol-water partition coefficient, expressed as K_{ow} in Figure 2, is determined by measuring the concentration of a particular compound in the water and the octanol phases after a period of mixing. It is important to note that the more hydrophobic the compound the less accurate the test, and the results should

<u>Octanol-Water Partition Coefficient</u>:

$$K_{ow} = \frac{\text{Concentration}_{\text{Octanol}}}{\text{Concentration}_{\text{Water}}}$$

Almost always presented as Log_{10} because the numbers are so large for hydrophobic compounds.

<u>Sorption Coefficient</u>:

$$K_p = \frac{\text{Concentration}_{\text{Solid Phase}}}{\text{Concentration}_{\text{Solution}}}$$

Units are $\frac{mg/kg}{mg/L}$, which is L/kg.

<u>Carbon Normalized Sorption Coefficient</u>:

$$K_{oc} = \frac{\text{Sorption Coefficient, } K_p}{\text{Fraction Organic Carbon}}$$

Figure 2. Relationships Pertinent to Nonpolar Organic Contaminant Transport

be viewed accordingly. It is often sufficient to know that an extremely high coefficient means that the compound is very hydrophobic. Since measured K_{ow} values can be in the millions for important environmental contaminants (PCB's, chlorinated pesticides, dioxins and furans), they are often expressed as the base10 logarithm, Log K_{ow}.

The K_{ow} has two attributes that make it especially useful in environmental assessments. First, it varies in a predictable way within classes of organic compounds. For example, as shown in Figures 3 and 4, if K_{ow} is known for one member of a class of compounds it can be used reasonably well to estimate a value for other members of the same family. In the examples shown, the K_{ow} can be correlated to the number of chlorine atoms or the number of rings in the molecular structure of classes of contaminants.

The second attribute results from the work of a number of agricultural and environmental researchers who correlated sorption on the organic matter of soils with the K_{ow} of the compounds involved. By using these attributes of the K_{ow}, it is possible to estimate the potential sorption of organic contaminants based on the structure of the compounds and the organic carbon content of the soil or aquifer material.

Sorption to Soils

Thus far it has been suggested that nonpolar organic compounds are sorbed by soils as a function of their hydrophobicity (K_{ow}) and the organic carbon content of the soil. There has been considerable research which suggests that the slow kinetics of the sorption process may be significant in swiftly moving ground water. Sorption studies using flow-through columns produce results sensitive to the flow rate, and batch tests indicate that

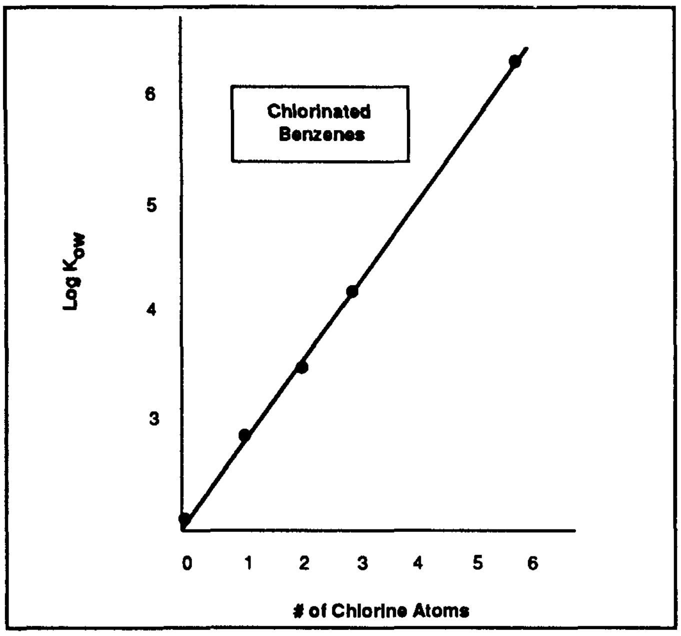

Figure 3. Relationship of Molecular Structure to Hydrophobic Character

increased sorption occurs with longer exposure times. The practical implication of these findings may be that sorption is overestimated in aquifer systems with relatively high flow rates.

Sorption is expressed in terms of a partition coefficient K_p, which is defined in Figure 2 as the ratio of the concentration of contaminants associated with the solid phase to that in solution, and is, therefore, conceptually similar to K_{ow}. The usefulness of K_{ow} in estimating sorption stems from the fact that the soil organic matter serves the same function as octanol in the octanol-water test. As a result, there have been many empirical relationships developed for estimating sorption from the K_{ow} and the soil organic carbon content. One expression, developed in the laboratory by Piwoni and Banerjee, 1989, for the sorption of common environmental contaminants with a low aquifer organic carbon, is:

$$\text{Log } K_{oc} = 0.69 \text{ Log } K_{ow} + 0.22$$

When applying such a relationship, it is important to select a study in which the compounds used are similar to those of interest at the site under investigation. However, as shown in Figure 5, even when applying the empirical relationship to a structurally dissimilar compound such as anthracene, if it is a nonpolar organic, the error of estimate should be less than a factor of five.

These estimates of sorption are based, in large measure, on a good evaluation of the soil organic carbon content at a site which is obtained from the degradation of naturally occurring organic matter. In this regard it is important to realize that soils and aquifer materials are very heterogeneous and the organic carbon content can vary considerably both in the vertical and horizontal dimension. Fortunately, this variability tends to be the greatest in the vertical soil profile while most site investigations are concerned with contaminant movement in the ground water away from the source. While the soil organic carbon content in the horizontal plane usually differs by a factor of ten or less, it can vary by a factor of 10 to 100 in the vertical dimension.

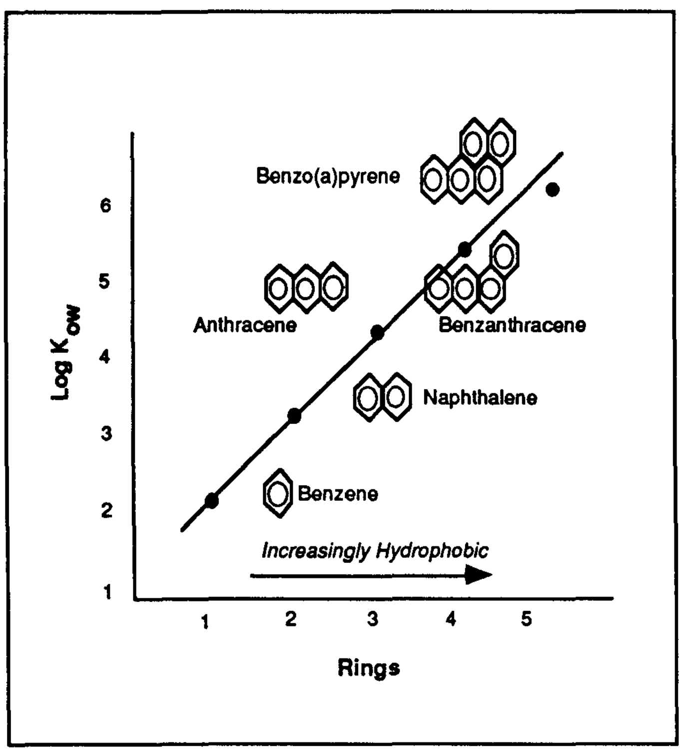

Figure 4. Relationship of Molecular Structure to Octanol Water Partition Coefficient

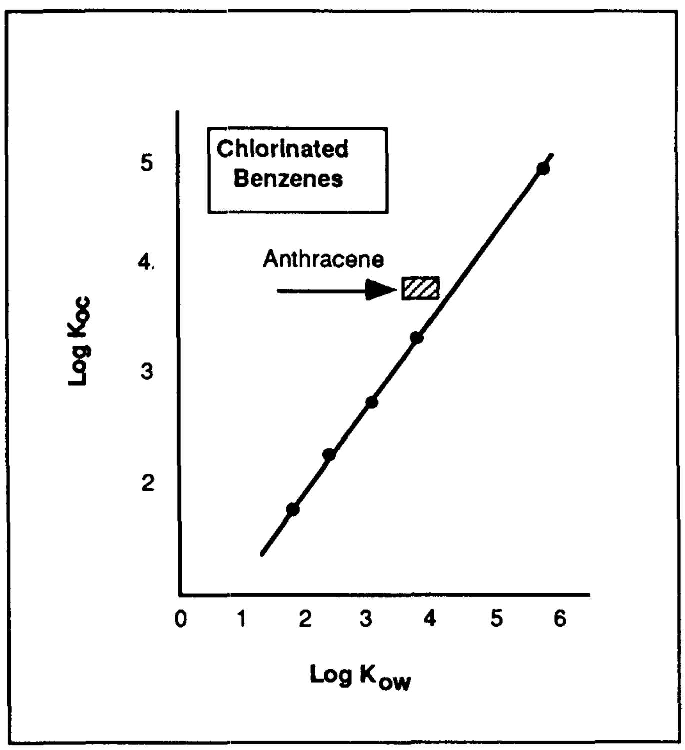

Figure 5. Partitioning on Soil Organic Carbon as Function of Octanol-Water Partition Coefficient

In order to determine the soil organic carbon content at a site, samples are usually obtained using split spoon sampler or other standard soil sampling devices. Representatives portions of the soil are then burned in an O_2 atmosphere and the produced CO_2 is measured by IR spectrophotometry. Before burning soil samples must be acidized to remove inorganic carbon. The accuracy of measuring organic carbon content can also be questionable, particularly at low levels and in carbonate soils. Existing analytical methods for measuring soil organic carbon were developed for the higher concentrations found near the surface. Therefore, at the low levels found in deeper soils and ground water, the same quality assurance procedures used in determining contaminant levels in water should be followed in determining the subsurface organic carbon content.

The processes driving hydrophobic sorption are nonspecific and depend upon small amounts of energy gained by moving contaminants out of the aqueous phase. The extent to which the process proceeds is dependent upon how receptive the soil matrix is to the organic molecule, which is a function of the organic content. But even when the organic carbon content is very low, some sorption of the most hydrophobic molecules continues because of the soil's mineral surfaces.

Sorption Estimation

In order to use the information provided above in estimating the amount of a contaminant associated with the aqueous and solid phases of an aquifer, it is necessary to develop a contamination scenario. To that end it is assumed that the contaminant at an industrial landfill is 1,4-dichlorobenzene, and there is sufficient data to indicate that: (1) most of the contamination is below the water table; (2) the contaminant concentration in ground water averages 1 mg/l; (3) the measured soil organic carbon is 0.2 percent; and (4) the pore water occupies 50 percent of the aquifer volume. Steps leading to an estimate of the contaminant's distribution between the aqueous and solid phases are:

Field Measurements:

Average contaminant concentration in monitoring wells = 1.0 mg/l

Soil organic carbon = 0.2 percent, therefore f_{oc} = 0.002

Pore water occupies 50 percent of the aquifer's volume.

From The Literature:

Log K_{ow} (1,4-dichlorobenzene) = 3.6

Piwoni and Banerjee Regression, Log K_{oc} = 0.69 K_{ow} + 0.22

Calculated:

Log K_{oc} = 0.69(3.6) + 0.22 = 2.70

therefore: K_{oc} = 506

$$K_p = K_{oc}(f_{oc}) = 506\ (0.002) \approx 1.0 \approx \frac{\text{Sorbed C}}{\text{Solution C}}$$

Conclusion;

The contaminant, equally distributed between each phase, is expressed as mg/kg (soil) and mg/l (water). Since soil is about 2.5 times more dense than water, 2 liters of aquifer would contain 1 liter of water and 2.5 kg of soil. Therefore, 1.0 mg/l of the contaminant would be associated with the water and 2.5 mg (70 percent) would be sorbed to the aquifer's solid phase.

As can be seen from this example, sorption tends to complicate remediation techniques that require pumping water to the surface for treatment. The desorption process has kinetic constraints that can render a pump-and-treat system ineffective. Slow desorption kinetics result in progressively lower contaminant concentrations at the surface, and less cost-effective contaminant removal. It is not uncommon to pump a system until the contaminant concentration in the pumped water meets a mandated restoration level, while the aquifer's solid phase still contains a substantial mass of contaminant. If the pumps are turned off, concentrations in the ground water will soon return to their equilibrium level.

Measuring Sorption

It is preferable to obtain the best information possible on which to base an estimate of sorption. Therefore, tests should be made with the contaminants of concern, as well as soils and aquifer material from a specific site. The goal is to obtain a partition coefficient, K_p, for use in the prediction of contaminant movement.

There are essentially two methods for measuring the partition coefficient, those being batch and dynamic techniques. Batch techniques are quicker and easier to perform and, therefore, more amenable to replication and quality control. Dynamic or flow through techniques offer the advantage of more closely representing processes occurring in the field.

The standard approach to determine the partition coefficient is to generate a sorption isotherm, a graphical representation of the amount of material sorbed at a variety of solute concentrations. The Freundlich isotherm, $S = K_pC^{1/n}$, is the representation most often used for the sorption of nonpolar organics to soils and aquifer materials. In this equation, S is the mass sorbed per mass of sorbent (mg/kg), C is the solute concentration at equilibrium (mg/l), K_p is the Freundlich partition coefficient, and 1/n is a fitting factor. The equation can be expressed in a linear form for convenience:

$$\text{Log } S = \text{Log } K_p + 1/n \text{ Log } C$$

As shown in Figure 6, Log K_p can be estimated by determining the intercept of the regression of a Log-Log plot of S and C.

Summary

This has been a discussion of the concepts involved in estimating contaminant sorption, particularly nonpolar organics, at hazardous waste sites. After determining the types of contaminants present at a site, it is possible to estimate K_p using K_{ow} values from the literature, an appropriate sorption coefficient/K_{ow} regression equation, and some organic carbon values.

If sorption determinations are within the scope of the project, site representative soil samples and contaminants should be selected

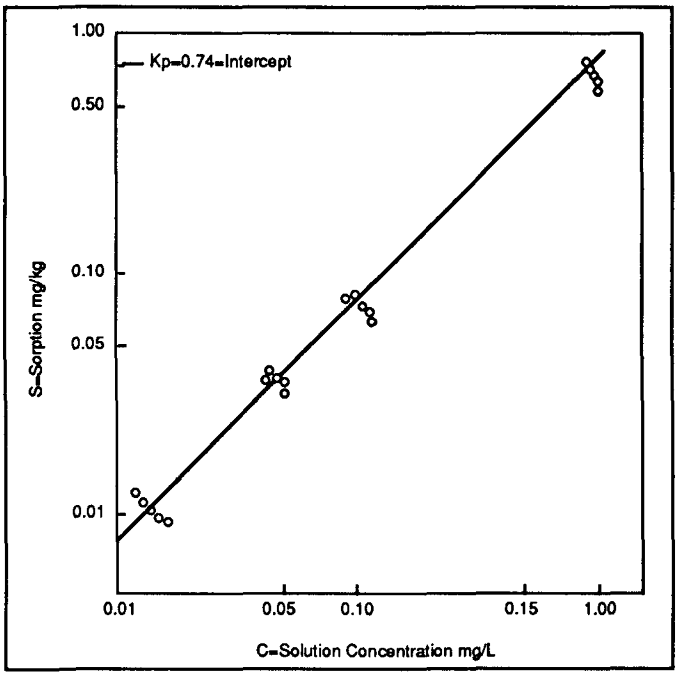

Figure 6. Sorption of 1,4-Dichlorobenzene

from the tests. The measured sorption information is best used to evaluate the validity of preliminary estimates. If the measured partition coefficients differ from the estimates by more than a factor of 2 or 3, it may be useful to select other contaminants from the site and determine K_p values the same soil samples. A plot of K_p values versus K_{ow} values will provide a useful guide for predicting the sorption characteristics of other contaminants at the site.

Selected References

American Society of Agronomy Soil Sciences of America. 1982. Methods of Soil Analyses. Part 2-Chemical and Microbiological Properties-Second Addition. Agronomy No. 9, Part 2.

Ballard, T.M. 1971. Role of Humic Carrier Substances in DDT Movement Through Forrest Soil. Soil Sci. Soc. Am. Proc. 35:145-147.

Banerjee, P., M.D. Piwoni, and K. Ebeid. 1985. Sorption of Organic Contaminants to Low Carbon Substrate Core. Chemosphere 14:1057-1067.

Bouchard, D.C., R.M. Powell, and D.A. Clark. 1988. Organic Cation Effects on the Sorption of Metals and Neutral Organic Compounds on Aquifer Material. J. Environ. Sci. Health Part A 23:585-601.

Bouchard, D.C., and A.L. Wood. 1988. Pesticide Sorption on Geologic Material of Varying Organic Carbon Content. Toxic. Industr. Health 4:341-349.

Briggs, G.G. 1981. Theoretical and Experimental Relationships Between Soil Adsorption, Octanol-Water Partition Coefficients, Water Solubilities, Bioconcentration Factors, and the Parachor. J. Agric. Food Chem. 29:1050-1059.

Brown, D.S., and E.W. Flagg. 1981. Empirical Prediction of Organic Pollutant Sorption in Natural Sediments. J. Environ. Qual. 10:382-386.

Carlson, D.J., L.M. Mayer, M.L. Brann, and T.H. Mague. 1985. Binding of Monomeric Organic Compounds to Macromolecular Dissolved Organic Matter In Seawater. Mar. Chem. 16:141-163.

Carlson, R.M., R.E. Carlson, and H.L. Kopperman. 1975. Determination of Partition Coefficients by Liquid Chromatography. J. Chromatogr. 107:219-223.

Caron, G., H. Suffet, and T. Belton. 1985. Effect of Dissolved Organic Carbon on the Environmental Distribution of Nonpolar Organic Compounds. Chemosphere 14:993-1000.

Carter, C.W., and I.H. Suffet. 1982. Binding of DDT to Dissolved Humic Materials. Environ. Sci. Technol. 16:735-740.

Chin, Y., W.J. Weber, and T.C. Voice. 1986. Determination of Partition Coefficients and Aqueous Solubilities by Reverse Phase Chromatography-II. Water Res. 20:1443-1450.

Chiou, C.T., R.L. Malcolm, T.I. Brinton, and D.E. Kile. 1986. Water Solubility Enhancement of Some Organic Pollutants and Pesticides by Dissolved Humic and Fulvic Acids. Environ. Sci. Technol. 20:502-508.

Dragun, James. 1988. The Soil Chemistry of Hazardous Materials. Hazardous Materials Control Research Institute. Silver Spring, MD.

Enfield, C.G. 1985. Chemical Transport Facilitated by Multiphase Flow Systems. Water Sci. Technol. 17:1-12.

Enfield, C.G., D.M. Walters, R.F. Carsell, and S.Z. Cohen. 1982. Approximating Transport of Organic Pollutants to Groundwater. Ground Water 20:711-722.

Garbarini, D.R., and L.W. Lion. 1986. Influence of the Nature of Soil Organics on the Sorption of Toluene and Trichloroethylene. Environ. Sci. Technol. 20:1263-1269.

Gamerdinger, A.P. R.J. Wagonet, and M. th. van Genuchten. 1990. Application of Two-Site/Two-Region Models for Studying Simultaneous Transport and Degradation of Pesticides. Soil Sci. Soc. Am. J. 54:957-963.

Gauthier, T.D., W.R. Seitz, and C.L. Grant. 1987. Effects of Structural and Compositional Variations of Dissolved Humic Materials on Pyrene K_{oc} Values. Environ. Sci. Technol. 21:243-248.

Griffin, R.A. and W.R. Roy. 1985. Interaction of Organic Solvents with Saturated Soil-Water Systems. Open File Report prepared for the Environmental Institute for Waste Management Studies, University of Alabama.

Gschwend, P.M., and S. Wu. 1985. On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants. Environ. Sci. Technol. 19:90-96.

Hassett, J.P., and M.A. Anderson. 1982. Effect of Dissolved Organic Matter on Adsorption of Hydrophobic Organic Compounds by River-and Sewage-Borne Particulate Matter. Water Res. 16:681-686.

Karickhoff, S.W. 1981. Semi-Empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils. Chemosphere 10:833-846.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Res. 13:241-248.

Landrum, P.F., S.R. Nihart, B.J. Eadie, and W.S. Gardner. 1984. Reverse-Phase Separation Method for Determining Pollutant Binding to Aldrich Humic Acid and Dissolved Organic Carbon of Natural Waters. Environ. Sci. Technol. 18:187-192.

McCarty, P.L., M. Reinhard, and B.E. Rittman. 1981. Trace Organics in Groundwater. Environ. Sci. Technol. 15:40-51.

Morrow, N.R., and I. Chatzis. 1982. Measurement and Correlation of Conditions for Entrapment and Mobilization of Residual Oil. DOE/BC/10310-20.

Mortland, M.M., S. Shaobai, and S.A. Boyd. 1986. Clay-Organic Adsorbents for Phenol and Chlorophenol. Clays and Clay Minerals. 34:581-585.

Piwoni, M.D., and P. Banerjee. 1989. Sorption of Volatile Organic Solvents from Aquifer Solution onto Subsurface Solids. Journal of Contaminant Hydrology. 4:163-179.

Poirrier, M.A., B.R. Bordelon, and J.L. Laseter. 1972. Adsorption and Concentration of Dissolved Carbon-14 DDT by Coloring Colloids in Surface Waters. Environ. Sci. Technol. 6:1033-1035.

Rao, P.S.C., and R.E. Jessup. 1983. Sorption and Movement of Pesticides and other Toxic Substances in Soils. p. 183-201. In D.W. Nelson et al. (ed.) Chemical Mobility and Reactivity in Soil Systems. SSA Spec. Publ. II, Madison, WI.

Schwarzenbach, R.P. and J. Westall. 1981. Transport of Nonpolar Organic Compounds from Surface Water to Groundwater. Laboratory Sorption Studies. Environ. Sci. Technol. 15:1360-1367.

Thurman, E.M. 1985. Humic Substances in Groundwater. p. 87-103. In G.R. Aiken et al. (ed.) Humic Substances in Soil, Sediment, and Water. Wiley-Interscience, New York.

Voice, T.C., C.P. Rice, and W.J. Weber, Jr. 1983. Effect of Solids Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems. Environ. Sci. Technol. 17:513-518.

Weber, W.J., Y. Chin, and C.P. Rice. 1986. Determination of Partition Coefficients and Aqueous Solubilities by Reverse Phase Chromatography-I. Water Res. 20:1433-1442.

Wershaw, R.L., P.J. Burcar, and M.C. Goldberg. 1969. Interaction of Pesticides with Natural Organic Material. Environ. Sci. Technol. 3:271-273.

Whitehouse, B. 1985. The Effects of Dissolved Organic Matter on the Aqueous Partitioning of Polynuclear Aromatic Hydrocarbons. Estuarine Coastal Shelf Sci. 20:393-402.

Wilson, J.L., and S.H. Conrad. 1984. Is Physical Displacement of Residual Hydrocarbons a Realistic Possibility in Aquifer Restoration? p. 274-298. In Proc. Petroleum Hydrocarbons Organic Chemicals Groundwater, Houston, TX.

Wolfe, T.A., T. Demiral, and E.R. Baumann. 1985. Interaction of Aliphatic Amines with Montmorillonite to Enhance Adsorption of Organic Pollutants. Clays and Clay Minerals. 33:301-311.

☆U.S. GOVERNMENT PRINTING OFFICE: 1991 - 548-187/20538

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use $300

EPA/540/4-90/053

REFERENCES CITED

49 CFR, 1982. Code of Federal Regulations, 49, Parts 100 to 177, October 1, 1982, pp. 231.

Acker, W. L. 1974. Basic Procedures for Soil Sampling and Core Drilling. Acker Drill Co., Inc., Scranton, PA, 246 pp.

Arneth, J.-D., G. Milde, H. Kerndorff, and R. Schleyer. 1988. Waste deposit influences on groundwater quality as a tool for waste type and site selection for final storage quality. In: P. Baccini (Ed.) The Landfill: Reactor and Final Storage, Swiss Workshop on Land Disposal of Solid Wastes, Gerzensee, March, 14-17, pp. 399-415.

Barcelona, M. J. 1989. Overview of the Sampling Process. In: Keith, L. H. (Ed.), Principles of Environmental Sampling, American Chemical Society, Washington, D.C., pp. 3-23.

Barth, D. S., B. J. Mason, T. H. Starks, and K. W. Brown. 1989. Soil Sampling Quality Assurance User's Guide (2nd edition), EPA 600/8-89/046, U.S. EPA, EMSL-LV, Las Vegas, NV, March, 225 pp.

Boucher, F. R. and G. F. Lee. 1972. Adsorption of Lindane and Dieldrin pesticides on unconsolidated aquifer sands. Env. Sci. Tech. 6:538-543.

Bouwer, E. J. 1984. Biotransformation of organic micropollutants in the subsurface. In: Petroleum Hydrocarbons and Organic Chemicals in Ground Water. National Well Water Association, Dublin, OH.

Cameron, R. E. 1963. Algae of southern Arizona - Part 1. Introduction to blue-green algae. Rev. Alg. N.S. 6(4):282-318.

Chiou, C. T. and T. D. Shoup. 1985. Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. Env. Sci. Tech. 19(12):1196-1200.

Chiou, C. T., D. E. Kile, and R. L. Malcolm. 1988. Sorption of vapors of some organic liquids on soil humic acid and its relation to partitioning of organic compounds in soil organic matter. Env. Sci. Tech. 22(3):298-303.

Dean, J. D., P. S. Huyakorn, A. S. Donigan, Jr., K. A. Voos, R. W. Schanz, Y. J. Meeks, and R. F. Carsel. 1989. Risk of Unsaturated/Saturated Transport and Transformation of Chemical Concentrations (RUSTIC) - Volume I: Theory and Code Verification, EPA/600/3-89/048a, Environmental Research Laboratory, U.S. EPA, Athens, GA, 203 pp.

Devitt, D. A., R. B. Evans, W. A. Jury, T. H. Starks, B. Eklunk, and A. Gholson. 1987. Soil Gas Screening for Detection and Mapping of Volatile Organics. National Well Water Association, Dublin, OH, 270 pp.

Farmer, W. J., M.-S. Yang, J. Letey, and W. S. Spencer. 1980. Land Disposal of Hexachlorobenzene Wastes: Controlling Vapor Movement in Soils. EPA-600/2-80-119, U.S. EPA, Environmental Research Laboratory, Cincinnati, OH, August 1980.

Gillman, R. W. and S.F. O'Hannesin. 1990. Sorption of aromatic hydrocarbons by materials used in construction of ground-water sampling wells. In: D. M. Nielsen and A. I. Johnson (eds.), Ground Water and Vadose Zone Monitoring, ASTM STP 1053, American Society of Testing Materials, Philadelphia, PA, pp. 108-122.

Hanisch, R. C. and M. A. McDevitt. 1984. Protocols for Sampling and Analysis of Surface Impoundments and Land Treatment/ Disposal Sites for VOCs. Technical Note. EPA-EMB 68-02-3850, Work Assignment 11.

Jamison, V. W., R. L. Raymond, and J. O. Hudson. 1975. Biodegradation of high-octane gasoline. In: Proceedings of the Third International Biodegradation Symposium. Applied Science Publishers Ltd., London.

Johnson, R. E. 1976. Degradation of DDT by Fungi. ResiDue Review 61:1-28.

Jury, W. A. 1984. A User's Manual for the Environmental Fate Screening Model Programs BAM and BCM, Dept. Soil and Environ. Sci., Univ. of California, Riverside, CA. Submitted to the California Department of Health Services.

Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

Kleopfer, R. D. et al. 1985. Anaerobic degradation of trichloroethylene in soil. Env. Sci. Tech. 19:277-284.

Kobayashi, H. and B. E. Rittman. 1982. Microbial removal of hazardous organic compounds. Env. Sci. Tech. 16(3):170A-183A.

Lechevalier, H. A. and M. P. Lechevalier. 1976. Actinomycetes found in sewage treatment plants of the activated sludge type. In: Actinomycetes: The Boundry Microorganisms, Toppen Co., Ltd., Tokyo, Japan.

Lewis, T. E., B. A. Deason, C. L. Gerlach, and D. W. Bottrell. 1990. Performance evaluation materials for the analysis of volatile organic compounds in soil: A preliminary assessment. J. Env. Sci. Health A25(5):505-531.

Lewis, T. E. and J. R. Parolini. 1991. Temperature and pressure fluctuations in air shipped samples: Implications on sample integrity. Analyst (in preparation).

Lotse, E. G., D. A. Graetz, G. Chesters, G. B. Lee, and L. W. Newland. 1968. Lindane adsorption by lake sediments. Env. Sci. Tech. 2:353-357.

Maskarinec M. P., 1990 Personal Communication.

Maskarinec, M. P., L. H. Johnson, S. K. Holladay. 1988. Preanalytical holding times. Paper presented at the Quality Assurance in Environmental Measurements Meeting, U.S. Army Toxic and Hazardous Materials Agency, Baltimore, MD, May 25-26, 1988.

McCoy, D. E. 1985. "301" studies provide insight into future of CERCLA. The Hazardous Waste Consultant 3/2:18-24.

Plumb, R. H., Jr. 1987. A practical alternative to the RCRA organic indicator parameters. In: T. Bursztynsky (Ed.) Proceedings of Hazmacon 87, Santa Clara, CA, April 21-23, pp. 135-150.

Plumb, R. H., Jr., and A. M. Pitchford. 1985. Volatile organic scans: Implications for ground water monitoring. Paper presented at the National Water Well Association/American Petroleum Institute Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, TX, November 13-15, 1985.

Richardson, E. M. and E. Epstein. 1971. Retention of three *insecticides on different size soil particles suspended in water.* Soil Sci. Soc. Am. Proc. 35:884-887.

Roy, W. R. and R. A. Griffin. 1985. Mobility of organic solvents in water-saturated soil materials, Environ. Geol. Wat. Sci. 7(4):241-247.

Shen, T. T. and G. H. Sewell. 1982. Air pollution problems of uncontrolled hazardous waste sites. In: Proceedings of 1982 Superfund Conference, Hazardous Materials Control Research Institute, Washington, pp. 76-80.

Siegrist, R. L. 1990. Volatile organic compound measurements in contaminated soils: The state of practice, methods development, and implications for remediation projects. J. Haz. Mat. (in press).

Siegrist, R. L. and P. D. Jennsen. 1990. Evaluation of sampling method effects on volatile organic compound measurements in contaminated soils. Env. Sci. Tech. 24:1387-1392.

Smith, J. A., C. T. Chiou, J. A. Kammer, and D. E. Kile. 1990. Effect of soil moisture on the sorption of trichloroethene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. Env. Sci. Tech. 24:676-683.

Spencer, W. F. and M. M. Cliath. 1970. Soil Sci. Soc. Am. Proc. 34:574-579.

Spencer, W. F., M. M. Cliath, W. A. Jury, and L.-Z. Zhang. 1988. Volatilization of organic chemicals from soil as related to their Henry's Law constants. J. Env. Qual. 17(3):504-509.

Stuart, J. D., V. D. Roe, W. M. Nash, and G. A. Robbins. 1990. Manual headspace method to analyze for gasoline contamination of ground water by capillary column gas chromatography. Personal Communication.

U.S. EPA. 1982. Test Method 624 (Purgeables). Methods for Organic Chemical Analysis of Municipal and Industrial Wastes, EPA-600/4-82-057, U.S. EPA Environmental Support Laboratory, Cincinnati, OH.

U.S. EPA. 1983. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II - Available Sampling Methods. EPA-600/4-83-040.

U.S. EPA. 1986a. Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units, EPA/530/-SW-86-040, pp 11-62.

U.S. EPA. 1986b. Test Methods for Evaluating Solid Waste (SW-846), Method 8240, Off. Solid Waste and Emergency Response (3rd Edition).

U.S. EPA. 1987. Data Quality Objectives for Remedial Response Activities: Development Process. EPA/540/G-87/003, Off. Solid Waste and Emergency Response, Washington, D.C.

U.S. EPA. 1988. *Field Screening Method Catalog User's Guide.* EPA/540/2-88/005, Sept. 1988, Office of Emergency and Remedial Response, Washington, D.C.

U.S. EPA. 1991a. Investigation of Sample and Sample Handling Techniques for the Measurement of Volatile Organic Compounds in Soil. University of Nevada, Las Vegas, submitted to U.S. EPA, Environmental Monitoring Systems Laboratory, Las Vegas, NV (in preparation).

U.S. EPA. 1991b. Manual for Sampling Soils for Volatile Organic Compounds. Environmental Monitoring Systems Laboratory, Las Vegas, NV, 26 pp. (in preparation).

van Ee, J. J., L. J. Blume, and T. H. Starks. 1990. A Rationale for the Assessment of Errors in the Sampling of Soils, EPA/600/4-90/013, Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV, 57 pp.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, New York, NY (2nd Edition).

Vogel, T. M. and P. L. McCarty. 1985. Biotransformation of *tetrachloroethylene to trichloroethylene, dichloroethylene,* vinyl chloride, and carbon dioxide under methanogenic conditions. Appl. Environ. Microbiol. 49:1080-1084.

Voice, T. C. and W. J. Weber, Jr. 1983. Sorption of hydrophobic compounds by sediments, soils, and suspended solids - I. Theory and background. Wat. Res. 17(10):1433-1441.

Wolf, D. C., T. H. Dao, H. D. Scott, and T. L. Lavy. 1989. Influence of sterilization methods on selected soil microbiological, physical, and chemical properties. J. Env. Qual. 18:39-44.

☆U.S. GOVERNMENT PRINTING OFFICE: 1991 - 548-187/25633

Agency

Cincinnati OH 45268-1072

POSTAGE & FEES PAID
EPA
PERMIT No. G-35

Official Business
Penalty for Private Use, $300

Please make all necessary changes on the above label, detach or copy, and return to the address in the upper left-hand corner

If you do not wish to receive these reports CHECK HERE □, detach, or copy this cover, and return to the address in the upper left-hand corner

EPA/540/4-91/001

three phases. The interactions between these phases are illustrated in Figure 1. The phase distribution is controlled by VOC physicochemical properties (e.g., solubility, Henry's constant), soil properties, and environmental variables (e.g., soil temperature, water content, organic carbon content).

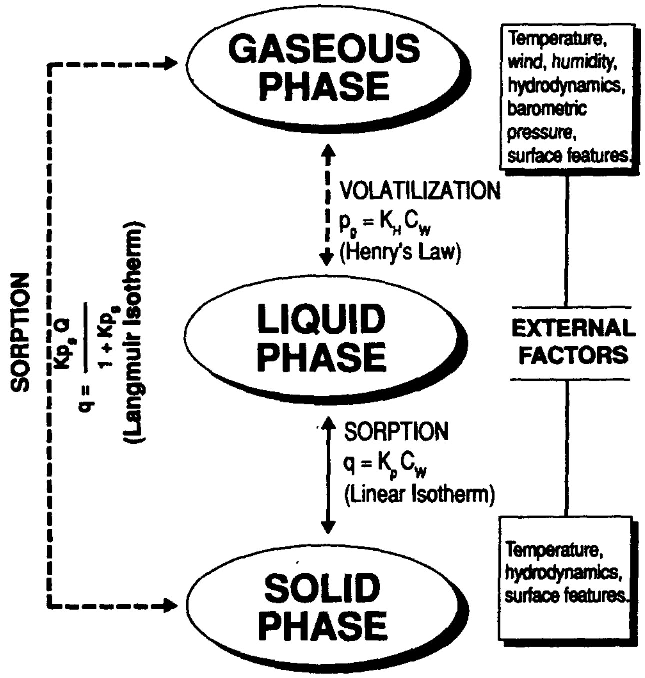

Figure 1. Equilibrium relationships for phase partitioning of VOCs in soil systems. See Table 2 for definitions of abbreviations.

The factors that affect the concentration and retention of VOCs in soils can be divided into five categories: VOC chemical properties, soil chemical properties, soil physical properties, environmental factors, and biological factors. A brief summary of VOC, soil, and environmental factors is presented in Table 2, which provides an overview of the factors that interact to control VOCs in the soil environment at the time a sample is collected. The cited references provide a more detailed discussion. The chemical and physical properties of selected VOCs are further described in Table 3. Note that many of these properties have been determined in the laboratory under conditions (e.g., temperature, pressure) that may differ from those encountered in the field. Devitt et al. (1987) offers a more exhaustive list.

Many VOCs exhibit extreme mobilities, particularly in the vapor phase, where their gas diffusion coefficients can be four times greater than their liquid diffusion coefficients. The vapor phase migration is influenced by the moisture content of the soil which alters the air-filled to water-filled pore volume ratio. The retention of VOCs by soil is largely controlled by reactions with the solid phase. This retention is especially true for the finer particles of silts and clays. The fine-grained particles (<2 mm) have a large surface-to-volume ratio, a large number of reactive sites, and high sorption capacities (Richardson and Epstein, 1971; Boucher and Lee, 1972; Lotse et al., 1968). Some investigators attribute the greater sorption of VOCs onto fine-grained particles to the greater organic carbon content of smaller particles (Karickhoff et al., 1979).

Soil-moisture content affects the relative contributions of mineral and organic soil fractions to the retention of VOCs (Smith et al., 1990). Mineral clay surfaces largely control sorption when soil moisture is extremely low (<1%), and organic carbon

(Continued on page 7)

TABLE 2. FACTORS AFFECTING VOC CONCENTRATIONS IN SOILS

Factor	Common Abbr.	Units	Effects on VOC Concentrations in Soil	References
VOC Chemical Properties				
Solubility	C_w	mg/L	Affects fate and transport in water, effects water/air partit., influences organic carbon partit.	Roy and Griffin (1985)
Henry's Constant	K_H	(atm-m³)/mole	Constant of proportionality between the water and gas phase concentrations; temperature and pressure dependent.	Shen and Sewell (1982) Spencer et al. (1988)
Vapor pressure	v.p.	mm Hg	Affects rate of loss from soil.	Shen and Sewell (1982)
Organic carbon part. coeff.	K_{oc}	mg VOC/g C	Adsorption coefficient normalized for soil organic content.	Farmer et al. (1980)
Octanol/water part. coeff.	K_{ow}	mg VOC/ mg octanol	Equilibrium constant for distribution of VOC between water and an organic (octanol) phase. Gives estimate of VOC partitioning into organic fraction of soil.	Voice and Weber (1983)
Boiling point	b.p.	°C	Affects co-evaporation of VOC and water from soil surface.	Voice and Weber (1983)
Soil/water distribution coefficient	K_d	[1]	Equilibrium constant for distribution of contaminant between solid and liquid phases.	Voice and Weber (1983)

(Continued)

TABLE 2. (CONTINUED)

Factor	Common Abbr.	Units	Effects on VOC Concentrations in Soil	References
Soil Chemical Properties				
Cation exchange capacity	CEC	meq/100 g	Estimates the number of negatively charged sites on soil particles where charged VOC may sorb; pH dependent.	
Ion concentration (activity)	pH	$-\log[H^+]$	Influences a number of soil processes that involve non-neutral organic partitioning; affects CEC and solubility of some VOCs.	
Total organic carbon content	TOC	mg C/g soil	An important partitioning medium for non-polar, hydrophobic (high K_{oc}) VOCs; sorption of VOCs in this medium may be highly irreversible.	Chiou et al. (1988) Farmer et al. (1980)
Soil Physical Properties				
Particle size or texture	A	% sand, silt, clay	Affects infiltration, penetration, retention, sorption, and mobility of VOCs. Influences hydraulics as well as surface-area-to-volume ratio (s.a.$\propto$Kd).	Richardson and Epstein (1971)
Specific surface area	s.a.	m^2/g	Affects adsorption of VOCs from vapor phase; affects soil porosity and other textural properties.	Karickhoff et al. (1979)
Bulk density	p_b	g/cm^3	Used in estimating mobility and retention of VOCs in soils; will influence soil sampling device selection.	Spencer et al. (1988)
Porosity	n	%	Void volume to total volume ratio. Affects volume, concentration, retention, and migration of VOCs in soil voids.	Farmer et al. (1980) Shen and Sewell (1982)
Percent moisture	Θ	% (w/w)	Affects hydraulic conductivity of soil and sorption of VOCs. Determines the dissolution and mobility of VOCs in soil.	Farmer et al. (1980) Chiou and Shoup (1985)
Water potential	pF	m	Relates to the rate, mobility, and concentration of VOCs in water or liquid chemicals.	
Hydraulic conductivity	K	m/d	Affects viscous flow of VOCs in soil water depending on degree of saturation, gradients, and other physical factors.	
Environmental Factors				
Relative humidity	R.H.	%	Could affect the movement, diffusion, and concentration of VOCs; interrelated factors; could be site specific and dependent upon soil surface - air interface differentials.	Chiou and Shoup (1985)
Temperature	T	°C		
Barometric pressure		mm Hg		
Wind speed		knots	Relevant to speed, movement, and concentration of VOCs exposed, removed, or diffusing from soil surface.	
Ground cover		%	Intensity, nature, and kind, and distribution of cover could affect movement, diffusion rates, and concentration of VOCs.	

TABLE 3. CHEMICAL PROPERTIES OF SELECTED VOLATILE ORGANIC COMPOUNDS†

Compound	m.w. (g/mole)	Solubilities (mg/L @ 20°C)	log K_{oc}[a]	log K_{ow}[b]	K_H[c]	Vapor Pressure (mm @ 20°C)
Acetone	58	Miscible		-0.22	-0.24	270 (@ 30°)
Benzene	78	1780	1.91	2.11	0.22	76
Bromodichloromethane	164	7500	2.18	2.10		50
Bromoform	253	3190 (@ 30°)				6 (@ 25°)
Bromomethane	95	900	1.34	1.19	1.50	1250
2-Butanone	72	270000	1.56	0.26		76
Carbon disulfide	76	2300	1.80			260
Carbon tetrachloride	154	800	2.04	2.64	0.94	90
Chlorobenzene	113	500	2.18	2.84	0.16	9
Chloroethane	65	5740	1.40	1.54	0.61	1000
2-Chloroethylvinyl ether	107					
Chloroform	120	8000	1.46	1.97	0.12	160
Chloromethane	51	8348	0.78	0.91	1.62	3800
Dibromochloromethane	208	3300	2.45	2.24		15 (@10.5°)
1,2-Dichlorobenzene	147	100	2.62	3.38		1
1,3-Dichlorobenzene	147	123 (@ 25°)		3.38		
1,4-Dichlorobenzene	147	49 (@ 22°)		3.39		1
1,1-Dichloroethane	99	5500	1.66	1.79	0.18	180
1,2-Dichloroethane	99	8690	1.34	1.48	0.04	61
1,1-Dichloroethene	97	400				500
trans-1,2-Dichloroethene	97	600	1.56	2.06		200 (@ 14°)
1,2-Dichloropropane	113	2700		1.99		42
cis-1,3-Dichloropropene	110	2700				34 (@ 25°)
trans-1,3,-Dichloropropene	111	2800				43 (@ 25°)
Ethylbenzene	106	152	2.60	3.15		7
2-Hexanone	100	3500		1.38		2
Methylene chloride	85	20000	1.40	1.25		349
Methylisobutylketone	100	17000	1.34	1.46	0.002	6
Perchloroethylene	166	150	2.60	2.60	0.85	14
Styrene	104	300	2.61	2.95		5
1,1,2,2-Tetrachloroethane	168	2900	2.07	2.60		5
Tetrachloroethene	166	150	2.78	3.40		18 (@ 25°)
Toluene	92	515	2.18	2.69	0.27	22
1,1,1-Trichloroethane	133	4400	2.19	2.50	1.46	100
1,1,2-Trichloroethane	133	4500	2.14	2.07		19
Trichloroethylene	132	700	2.09	2.29	0.37	60
Trichlorofluoromethane	137	1100 (@ 25°)	2.68			687
Vinyl acetate	86	25000	1.59	0.73		115 (@ 25°)
Vinyl chloride	63	1100 (@ 25°)	2.60	1.38	97.0	2660 (@ 25°)
Total xylenes	106	198	2.46		9400.0	

† From Verschueren 1983, Jury 1984.
[a] Organic carbon partitioning coefficient.
[b] Octanol/water partitioning coefficient.
[c] Henry's Gas Law constant (dimensionless) @ 20°C.

TABLE 4. MICROBIOLOGICAL FACTORS AFFECTING VOCs IN SOIL SYSTEMS

Organism(s)	Compound(s)	Conditions	Remarks/metabolite(s)
Various soil microbes	Pentachlorophenol	Aerobic	tetra-, tri-, di-, and m-Chlorophenol (Kobayashi and Rittman, 1982)
	1,2,3- and 1,2,4-Trichlorobenzene	Aerobic	2,6-; 2,3-Dichlorobenzene; 2,4- and 2,5-dichlorobenzene; CO_2 (Kobayashi and Rittman, 1982)
Various soil bacteria	Trichloroethane, trichloromethane, methylchloride, chloroethane, dichloroethane, vinylidiene chloride, trichloroethene, tetrachloroethene, methylene chloride, dibromochloromethane, bromochloromethane	Anaerobic	Reductive dehalogenation under anoxic conditions, (i.e., < 0.35 V) (Kobayashi and Rittman, 1982)
Various soil microbes	Tetrachloroethene	Anaerobic	Reductive dehalogenation to trichloroethene,dichloroethene, and vinyl chloride, and finally CO_2 (Vogel and McCarty, 1985)
Various soil microbes	^{13}C-labeled trichloroethene	Anaerobic	Dehalogenation to 1,2-dichloroethene and not 1,1-dichloroethene (Kleopfer et al., 1985)
Various soil bacteria	Trichloroethene	Aerobic	Mineralized to CO_2 in the presence of a mixture of natural gas and air
Actinomycetes	chlorinated and non-chlorinated aromatics	aerobic	Various particle breakdown products mineralized by other microorganisms (Lechevalier and Lechevalier, 1976)
Fungi	DDT	Aerobic	Complete mineralization in 10-14 days (Johnsen, 1976)
Pseudomonas sp. *Acinetobacter* sp. *Micrococcus* sp.	Aromatics	Aerobic	Organisms were capable of sustaining growth in these compounds with 100% biodegradation (Jamison et al., 1975)
Acetate-grown biofilm	Chlorinated aliphatics	Aerobic	No biodegration observed (Bouwer, 1984)
		Methanogenic	Nearly 100% biodegradation observed (Bouwer, 1984)
	Chlorinated and nonchlorinated aromatics	Aerobic	Nearly 100% biodegradation (Bouwer, 1984)
		Methanogenic	No biodegration observed (Bouwer, 1984)
Blue-green algae (cyanobacteria)	Oil wastes	Aerobic	Biodegradation of automobile oil wastes, crankcase oil, etc. (Cameron, 1963)

partitioning is favored when moisture content is higher (Chiou and Shoup, 1985).

Biological factors affecting VOC retention in soil systems can be divided into microbiological and macrobiological factors. On the microbiological level, the indigenous microbial populations present in soil systems can alter VOC concentrations. Although plants and animals metabolize a diversity of chemicals, the activities of the higher organisms are often minor compared to the transformations affected by heterotrophic bacteria and fungi residing in the same habitat. The interactions between environmental factors, such as dissolved oxygen, oxidation-reduction potential (Eh), temperature, pH, availability of other compounds, salinity, particulate matter, and competing organisms, often control biodegradation. The physical and chemical characteristics of the VOC, such as solubility, volatility, hydrophobicity, and K_{ow}, also influence the ability of the compound to biodegrade. Table 4 illustrates some examples of the microbiological alterations of some commonly encountered soil VOCs. In general, the halogenated alkanes and alkenes are metabolized by soil microbes under anaerobic conditions (Kobayashi and Rittman, 1982; Bouwer, 1984), whereas the halogenated aromatics are metabolized under aerobic conditions. To avoid biodegradation and oxidation of VOCs in soils, scientists at the U.S. EPA Robert S. Kerr Environmental Research Laboratory in Ada, OK, extrude the sample in a glove box.

On a macro scale, biological factors can influence the migration of VOCs in the saturated, vadose, and surface zones (Table 5). Biofilms may accumulate in the saturated zone and may biodegrade and bioaccumulate VOCs from the ground water. The biofilm, depending on its thickness, may impede ground-water flow. Plant roots have a complex microflora associated with them known as mycorrhizae. The mycorrhizae may enhance VOC retention in the soil by biodegradation or bioaccumulation. The root channels may act as conduits for increasing the migration of VOCs through the soil. Similarly, animal burrows and holes may serve as paths of least resistance for the movement of VOCs through soil. These holes may range from capillary-size openings, created by worms and nematodes, to large-diameter tunnels excavated by burrowing animals. These openings may increase the depth to which surface spills penetrate the soil. A surface covering consisting of assorted vegetation is a significant barrier to volatilization of VOCs into the atmosphere. Some ground-water and vadose-zone models (e.g., RUSTIC) include subroutines to account for a vegetative cover (Dean et al., 1989).

TABLE 5. MACROBIOLOGICAL FACTORS AFFECTING VOCs IN SOIL SYSTEMS

Factor	Zone	Effects
Biofilms	Saturated	Biodegradation, bioaccumulation, formation of metabolites that are more or less toxic than parent compound, thick biofilm may retard saturated flow
Plant roots	Capillary fringe to vadose	Mycorrihizal fungi may biodegrade or bioaccumulate VOC, root channels may serve as conduits for VOC migration
Animal burrows holes	Vadose	May act as entry point for and downward migration of surface spills and serve as conduit for upward VOC migration
Vegetative cover	Soil surface	Serve as barrier to volatilization from soil surface and retard infiltration of surface spills

SOIL SAMPLING AND ANALYSIS DESIGN

Prior to any sampling effort, the RPM or OSC must establish the intended purpose of the remedial investigation/feasibility study (RI/FS). The goals of collecting samples for VOA may include source identification, spill delineation, fate and transport, risk assessment, enforcement, remediation, or post-remediation confirmation. The intended purpose of the sampling effort drives the selection of the appropriate sampling approach and the devices to be used in the investigation.

The phase partitioning of the VOC can also influence which sampling device should be employed. Computer models generally are used only at the final stages of a RI/FS. However, modeling techniques can be used throughout the RI/FS process to assist in sampling device selection by estimating the phase partitioning of VOCs. The RPM is the primary data user for a RI/FS led by a federal agency. As such, the RPM must select the sampling methodology to be employed at the site. Figure 2 illustrates the sequence of events used to plan a VOC sampling and analysis activity.

The domains of interest also must be determined. The target domains may include surface (two dimensions) or subsurface (three dimensions) environments, hot spots, a concentration greater or less than an action limit, or the area above a leaking underground storage tank. Statistics that may be generated from the target domain data must be considered before a sample and analysis design is developed. Possible statistics of interest may include average analyte concentration and the variance about the mean (statistics that compare whether the observed level is significantly above or below an action level) as well as temporal and spatial trends. Data must be of sufficiently high quality to meet the goals of the sampling activity. The level of data quality is defined by the data quality objectives (DQOs). In RI/FS activities, sites are so different and information on overall measurement error (sampling plus analytical error) is so limited that it is not practical to set universal or generic precision, accuracy, representativeness, completeness, and comparability (PARCC) goals. The reader is referred to a user's guide on quality assurance in soil sampling (Barth et al., 1989) and a guidance document for the development of data quality objectives for remedial response activities (U.S. EPA, 1987).

DQOs are qualitative and quantitative statements of the level of uncertainty a decision maker is willing to accept in making decisions on the basis of environmental data. It is important to realize that if the error associated with the sample collection or

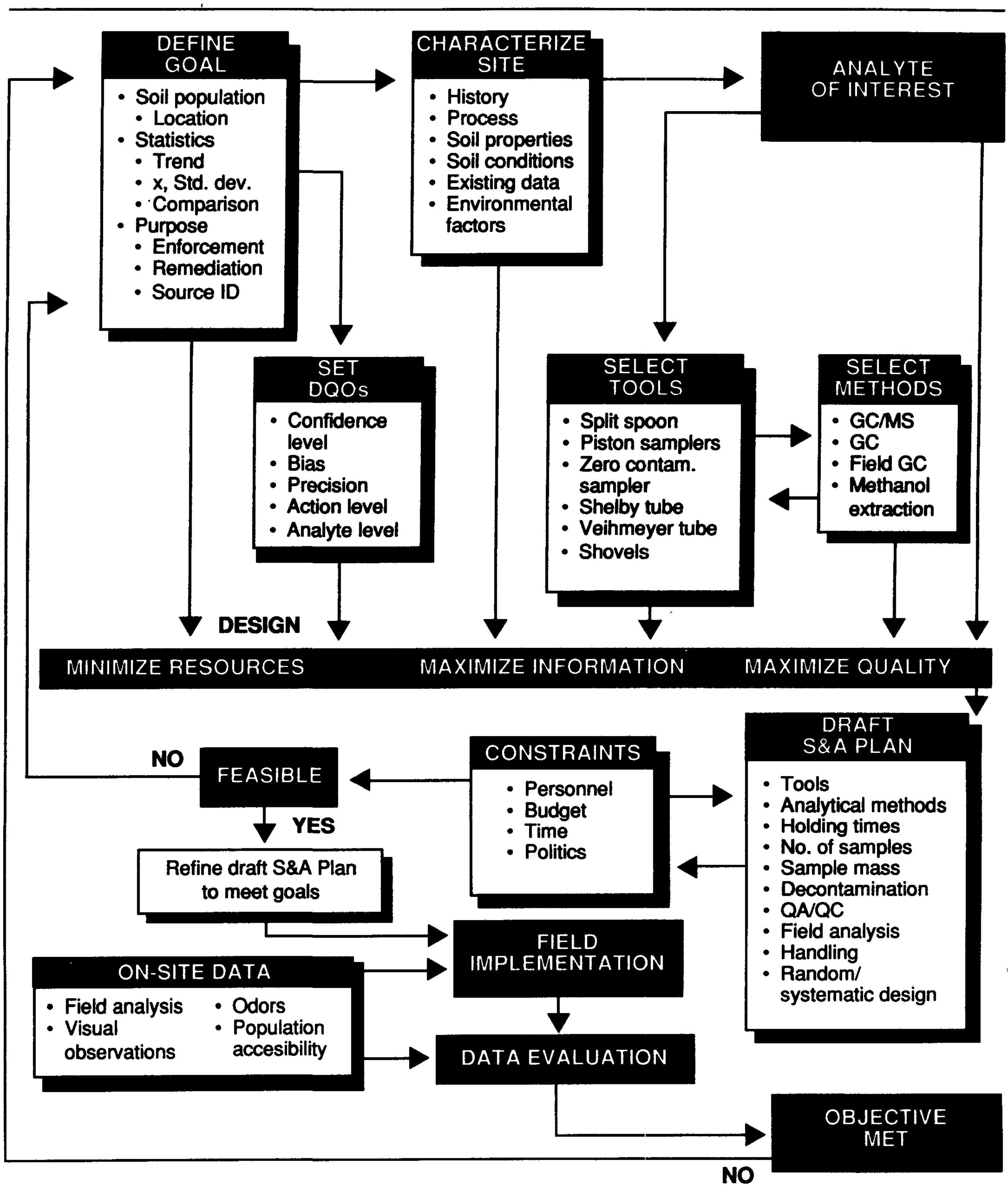

Figure 2. Flowchart for planning and implementation of a soil sampling and analysis activity.

preparation step is large, then the best laboratory quality assurance program will be inadequate (van Ee et al., 1990). The greatest emphasis should be placed on the phase that contributes the largest component of error. For the analysis of soils for VOCs, the greatest sources of error are the sample collection and handling phases.

The minimum confidence level (CL) required to make a decision from the data is defined by the DQOs. The minimum CL depends on the precision and accuracy in sampling and analysis and on the relative analyte concentration. Relative error may be reduced by increasing either the number or the mass of the samples to be analyzed. For instance, although 5-g aliquots collected in the field might exhibit unacceptable errors, 100-g samples will yield smaller errors and might therefore meet study or project requirements. Compositing soil samples in methanol in the field also can reduce variance by attenuating short-range spatial variability.

Field sampling personnel should coordinate with laboratory analysts to ensure that samples of a size appropriate to the analytical method are collected. For example, if the laboratory procedure for preparing aliquots calls for removing a 5-g aliquot from a 125-mL wide-mouth jar, as per SW-846, Method 8240 (U.S. EPA 1986b), then collecting a larger sample in the field will not reduce total measurement error, because additional errors will be contributed from opening the container in the laboratory and from subsequent homogenization. Aliquoting of a 5-g sample in the field into a 40-mL VOA vial that can be directly attached to the laboratory purge-and-trap unit significantly reduces loss of VOCs from the sample (U.S. EPA, 1991a). Significant losses of VOCs were observed when samples were homogenized as per Method 8240 specifications. Smaller losses were observed for smaller aliquots (1 to 5 g) placed in 40-mL VOA vials that had modified caps that allowed direct attachment to the purge-and-trap device. The procedure of collecting an aliquot in the field eliminates the need for sample preparation and eliminates subsequent VOC loss in the laboratory.

Field-screening procedures are gaining recognition as an effective means of locating sampling locations and obtaining real-time data. The benefits of soil field-screening procedures are: (1) near real-time data to guide sampling activities, (2) concentration of Contract Laboratory Program (CLP) sample collection in critical areas, (3) reduced need for a second visit to the site, and (4) reduced analytical load on the laboratory. Limitations of field-screening procedures are: (1) a priori knowledge of VOCs present at the site is needed to accurately identify the compounds, (2) methodologies and instruments are in their infancy and procedures for their use are not well documented and (3) a more stringent level of quality assurance and quality control (QA/QC) must be employed to ensure accurate and precise measurements. The potential benefits and limitations associated with soil-screening procedures must be carefully weighed and compared to the DQOs.

Certain sampling and analytical methods have inherent limitations on the type of QA/QC that is applicable. For example, splitting soil samples in the field would not be appropriate for VOA due to excessive analyte loss. The higher the minimum CL needed to make a decision, the more rigorous the QA/QC protocols must be. As VOC concentrations in the soil sample approach the action or detection limit, the quantity and frequency of QA/QC samples must be increased, or the number of samples must be increased, to ensure that the data quality obtained is appropriate to satisfy project objectives.

One critical element in VOC analysis is the appropriate use of trip blanks. If a sample consists of a silty clay loam, a trip blank of washed sand may not be realistic, for such a blank would not retain VOC cross contaminants in the same way as the sample. The trip blank soil matrix should have a sorptive capacity similar to the actual sample. In addition, high-concentration and low-concentration samples should be shipped in separate coolers.

DEVICE SELECTION CRITERIA

The selection of a sampling device and sampling procedures requires the consideration of many factors including the number of samples to be collected, available funds, soil characteristics, site limitations, ability to sample the target domain, whether or not screening procedures are to be used, the size of sample needed, and the required precision and accuracy as given in the DQOs. The number of samples to be collected can greatly affect sampling costs and the time required to complete a site characterization. If many subsurface samples are needed, it may be possible to use soil-gas sampling coupled with on-site analysis as an integrated screening technique to reduce the area of interest and thus the number of samples needed. Such a sampling approach may be applicable for cases of near-surface contamination.

Ultimately, the sampling, sample handling, containerizing, and transport of the soil sample should minimize losses of volatiles and should avoid contamination of the sample. Soil sampling equipment should be readily decontaminated in the field if it is to be reused on the job site. Decontamination of sampling equipment may require the use of decontamination pads that have impervious liners, wash and rinse troughs, and careful handling of large equipment. Whenever possible, a liner should be used inside the sampling device to reduce potential cross contamination and carryover. Decontamination procedures take time, require extra equipment, and ultimately increase site characterization costs. Ease and cost of decontamination are thus important factors to be considered in device selection.

Several soil-screening procedures are in use that include headspace analysis of soils using organic vapor analyzers: water (or NaCl-saturated water) extraction of soil, followed by static headspace analysis using an organic vapor analyzer (OVA) or gas chromatograph (GC); colorimetric test kits; methanol extraction followed by headspace analysis or direct injection into a GC; and soil-gas sampling (U.S. EPA, 1988). Field measurements may not provide absolute values but often may be a superior means of obtaining relative values. These procedures are gaining acceptance.

Site Characteristics

The remoteness of a site and the physical setting may restrict access and, therefore, affect equipment selection. Such factors as vegetation, steep slopes, rugged or rocky terrain, overhead power lines or other overhead restrictions, and lack of roads can contribute to access problems.

The presence of underground utilities, pipes, electrical lines, tanks and leach fields can also affect selection of sampling equipment. If the location or absence of these hazards cannot be established, it is desirable to conduct a nonintrusive survey of the area and select a sampling approach that minimizes hazards. For example, hand tools and a backhoe are more practical under such circumstances than a large, hollow-stem auger. The selection of a sampling device may be influenced by other contaminants of interest such as pesticides, metals, semivolatile organic compounds, radionuclides, and explosives. Where the site history indicates that the matrix is other than soil, special consideration should be given to device selection. Concrete, reinforcement bars, scrap metal, and lumber will affect sampling device selection. Under some circumstances, it may not be practical to collect deep soil samples. The presence of ordnance, drums, concrete, voids, pyrophoric materials, and high-hazard radioactive materials may preclude some sampling and may require development of alternate sampling designs, or even reconsideration of project objectives.

Soil Characteristics

The characteristics of the soil material being sampled have a marked effect upon the selection of a sampling device. An investigator must evaluate soil characteristics, the type of VOC, and the depth at which a sample is to be collected before selection of a proper sampling device. Specific characteristics that must be considered are:

1. Is the soil compacted, rocky, or rubble filled? If the answer is yes, then either hollow stem augers or pit sampling must be used.

2. Is the soil fine grained? If yes, use split spoons, Shelby tubes, liners, or hollow stem augers.

3. Are there flowing sands or water saturated soils? If yes, use samplers such as piston samplers that can retain these materials.

SOIL-GAS MEASUREMENTS

Soil-gas measurements can serve a variety of screening purposes in soil sampling and analysis programs, from initial site reconnaissance to remedial monitoring efforts. Soil-gas measurements should be used for screening purposes only, and not for definitive determination of soil-bound VOCs. Field analysis is usually by hand-held detectors, portable GC or GC/MS, infrared detectors, ion mobility spectrometers (IMS), industrial hygiene detector tubes, and, recently, fiber optic sensors.

At some sites, soil-gas sampling may be the only means of acquiring data on the presence or absence of VOCs in the soil. For example, when the size and density of rocks and cobbles at a site prevent insertion and withdrawal of the coring device and prevent sampling with shovels and trowels, unacceptable losses of VOCs would occur. Soil-gas measurements, which can be made on site or with collected soil samples, can be used to identify volatile contaminants and to determine relative magnitudes of concentration. Smith et al. (1990) have shown a disparity in soil-gas VOC concentrations and the concentration of VOCs found on the solid phase.

Soil-gas measurements have several applications. These include in situ soil-gas surveying, measurement of headspace concentrations above containerized soil samples, and scanning of soil contained in cores collected from different depths. These applications are summarized in Table 6. Currently, no

TABLE 6. APPLICATIONS OF SOIL-GAS MEASUREMENT TECHNIQUES IN SOIL SAMPLING FOR VOCs

Application	Uses	Methods	Benefits/limitations
Soil vapor surveying	Identify sources and extent of contamination. Distinguish between soil and ground water contamination. Detect VOCs under asphalt, concrete, etc.	Active sampling from soil probes into canisters, glass bulbs, gas sampling bags. Passive sampling onto buried adsorptive substrates. Followed by GC or other analysis.	BENEFITS: Rapid, inexpensive screening of large areas, avoid sampling uncontaminated areas. LIMITATIONS: False positives and negatives, miss detecting localized surface spills, disequilibrium between adsorbed and vapor phase VOC concentrations.
Soil headspace measurements	Screen large numbers of soil samples.	Measure headspace above containerized soil sample. Containers range from plastic sandwich bags to VOA vials. Use GC, vapor detectors, IMS, etc.	BENEFITS: More representative of adsorbed solid phase concentration. LIMITATIONS: Losses of vapor phase component during sampling and sample transfer.
Screening soil cores	Soil cores scanned to locate depth where highest VOC levels are located.	Collect core sample (e.g., unlined split spoon) and scan for vapors near core surface using portable vapor monitor.	BENEFITS: Locate and collect soil from hot spot in core for worst case. LIMITATIONS: False negatives and positives, environmental conditions can influence readings (e.g., wind speed and direction, temperature, humidity).

standard protocols exist for soil-gas analysis; many investigators have devised their own techniques, which have varying degrees of efficacy. Independently, the American Society for Testing and Materials (ASTM) and EPA EMSL-LV are preparing guidance documents for soil-gas measurement. These documents should be available late in 1991.

The required precision and accuracy of site characterization, as defined in the DQOs, affect the selection of a sampling device. Where maximum precision and accuracy are required, sampling devices that collect an intact core should be used, particularly for more volatile VOCs in nonretentive matrices. Augers and other devices that collect highly disturbed samples and expose the samples to the atmosphere can be used if lower precision and accuracy can be tolerated. Collection of a larger number of samples to characterize a given area, however, can compensate for a less precise sampling approach. The closer the expected contaminant level is to the action or detection limit, the more efficient the sampling device should be for obtaining an accurate measurement.

SOIL SAMPLING DEVICES

Table 7 lists selection criteria for different types of commercially available soil sampling devices based on soil type, moisture status, and power requirements. The sampling device needed to achieve a certain sampling and analysis goal can be located in Table 7 and the supplier of such a device can be identified in Table 8. Table 8 is a partial list of commercially available soil sampling devices that are currently in use for sampling soils for VOC analysis. The list is by no means exhaustive and inclusion

(Continued on page 14)

TABLE 7. CRITERIA FOR SELECTING SOIL SAMPLING EQUIPMENT†

Type of Sampler	Obtains Core Samples	Most Suitable Soil types	Operation in Stony Soils	Suitable Soil Moisture Conditions	Relative Sample Size	Labor Requirements (# of Persons)	Manual or Power Operation
A. Mechanical Sample Recovery							
1. Hand-held Power augers	No	Coh/coh'less	Unfavorable	Intermediate	Large	2+	Power
2. Solid stem flight augers	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
3. Hollow-stem augers	Yes	Coh/coh'less	Fav/unfav	Wet to dry	Large	2+	Power
4. Bucket augers	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
5. Backhoes	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
B. Samplers							
1. Screw-type augers	No	Coh	Unfavorable	Intermediate	Small	Single	Manual
2. Barrel augers							
a. Post-hole augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
b. Dutch augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
c. Regular barrel augers	No	Coh	Unfavorable	Intermediate	Large	Single	Manual
d. Sand augers	No	Coh'less	Unfavorable	Intermediate	Large	Single	Manual
e. Mud augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
3. Tube-type samplers							
a. Soil samplers	Yes	Coh	Unfavorable	Wet to dry	Small	Single	Manual
b. Veihmeyer tubes	Yes	Coh	Unfavorable	Intermediate	Large	Single	Manual
c. Shelby tubes	Yes	Coh	Unfavorable	Intermediate	Large	2+*	Both
d. Ring-lined samplers	Yes	Coh'less	Favorable	Wet to intermediate	Large	2+*	Both
e. Continuous samplers	Yes	Coh	Unfavorable	Wet to dry	Large	2+	Power
f. Piston samplers	Yes	Coh	Unfavorable	Wet	Large	2+*	Both
g. Zero-contamination samplers	Yes	Coh	Unfavorable	Wet to intermediate	Small	2+*	Both
h. Split spoon samplers	Yes	Coh	Unfavorable	Intermediate	Large	2+*	Both
4. Bulk samplers	No	Coh	Favorable	Wet to dry	Large	Single	Manual

† Adapted from U.S. EPA, 1986a.
* All hand-operated versions of samplers, except for continuous samplers, can be worked by one person.
Coh = cohesive.

TABLE 8. EXAMPLES OF COMMERCIALLY AVAILABLE SOIL SAMPLING DEVICES

Manufacturers	Sampling Device	Specifications Length (inches) I.D. (inches) Sampler Material	Liners	Features
Associated Design & Manufacturing Co. 814 North Henry Street Alexandria, VA 22314 703-549-5999	Purge and Trap Soil Sampler	3 0.5 Stainless steel		Will rapidly sample soils for screening by "Low Level" Purge and Trap methods.
Acker Drill Co. P.O. Box 830 Scranton, PA 717-586-2061	Heavy Duty "Lynac" Split Tube Sampler	18 & 24 1-1/2 to 4-1/2 Steel	Brass, stainless	Split tube allows for easy sample removal.
	Dennison Core Barrel	24 & 60 1-7/8 to 6-5/16	Brass	Will remove undisturbed sample from cohesive soils.
AMS Harrison at Oregon Trail American Falls, ID 83211	Core Soil Sampler	2 to 12 1-1/2 to 3 Alloy, stainless	Stainless, plastic aluminum, bronze teflon	Good in all types of soils.
	Dual Purpose Soil Recovery Probe	12, 18 &24 3/4 and 1 4130 Alloy, stainless	Butyrate, Teflon stainless	Adapts to AMS "up & down" hammer attachment. Use with or without liners.
	Soil Recovery Auger	8 to 12 2 & 3 Stainless	Plastic, stainless Teflon, aluminum	Adaptable to AMS extension and cross-handles.
Concord, Inc. 2800 7th Ave. N. Fargo, ND 58102 701-280-1260	Speedy Soil Sampler	48 & 72 3/16 to 3-1/2 Stainless	Acetate	Automated system allows retrieval of 24 in soil sample in 12 sec.
	Zero Contamination Unit Hand-Held Sampler			
CME Central Mine Equip. Co. 6200 North Broadway St. Louis, MO 63147 800-325-8827	Continuous Sampler	60 2-1/2 to 5-3/8 Steel, stainless	Butyrate	May not be suitable in stony soils. Adapts to CMS auger.
	Bearing Head Continuous Sample Tube System	60 2-1/2 Steel, stainless	Butyrate	Versatile system. Adapts to all brands of augers.
Diedrich Drilling Equip. P.O. Box 1670 Laporte, IN 46350 800-348-8809	Heavy Duty Split Tube Sampler	18 & 24 2, 2-1/2, 3 Steel	Brass, plastic stainless, Teflon	Full line of accessories are available.
	Continuous Sampler	60 3, 3-1/2	Brass, plastic stainless, Teflon	Switch-out device easily done.

(Continued)

TABLE 8. (CONTINUED)

Manufactures	Sampling Device	Specifications Length (inches) I.D. (inches) Sampler Material	Liners	Features
Geoprobe Systems 607 Barney St. Salina, KS 913-825-1842	Probe Drive Soil Sampler	11-1/4 0.96 Alloy steel		Remains completely sealed while pushed to depth in soil.
Giddings Machine Co. P.O. Drawer 2024 Fort Collins, CO 80522 303-485-5586	Coring Tubes	48 & 60 7/8 to 2-3/8 4130 Molychrome	Butyrate	A series of optional 5/8 in slots permit observation of the sample.
JMC Clements and Associates R.R. 1 Box 186 Newton, IA 50208 800-247-6630	Environmentalist's Sub-soil Probe	36 & 48 0.9 Nickel plated	PETG plastic, stainless	Adapts to drop-hammer to penetrate the hardest of soils.
	Zero Contamination Tubes	12, 18 & 24 0.9 Nickel plated	PETG plastic, stainless	Adapts to power probe.
Mobile Drilling Co. 3807 Madison Ave. Indianapolis, IN 46227 800-428-4475	"Lynac" Split Barrel Sampler	18 & 24 1-1/2	Brass, plastic	Adapts to Mobile wireline sampling system.
Solitest, Inc. 66 Albrecht Drive Lake Bluff, IL 800-323-1242	Zero Contamination Sampler	12, 18 & 24 0.9 Chrome plated	Stainless, acetate	Hand sampler good for chemical residue studies.
	Thin Wall Tube Sampler (Shelby)	30 2-1/2, 3, 3-1/2 Steel		Will take undisturbed samples in cohesive soils and clays.
	Split Tube Sampler	24 1-1/2 to 3 Steel	Brass	Forced into soil by jacking, hydraulic pressure or driving. Very popular type of sampler.
	Veihmeyer Soil Sampling Tube	48 & 72 3/4 Steel		Adapts to drop hammer for sampling in all sorts of soils.
Sprague & Henwood, Inc. Scranton, PA 18501 800-344-8506	S & H Split Barrel Sampler	18 & 24 2 to 3-1/2	Brass, plastic	A general all-purpose sampling device designed for driving into material to be sampled.

Note: This list is not exhaustive. Inclusion in this list should not be construed as endorsement for use.

in the list should not be construed as an endorsement for their use.

Commonly, soil samples are obtained from the near surface using shovels, scoops, trowels, and spatulas. These devices can be used to extract soil samples from trenches and pits excavated by back hoes. A precleaned shovel or scoop can be used to expose fresh soil from the face of the test pit. A thin-walled tube or small-diameter, hand-held corer can be used to collect soil from the exposed face. Bulk samplers such as shovels and trowels cause considerable disturbance of the soil and expose the sample to the atmosphere, enhancing loss of VOCs. Siegrist and Jenssen (1990) have shown that sampling procedures that cause the least amount of disturbance provide the greatest VOC recoveries. Therefore, sampling devices that obtain undisturbed soil samples using either hand-held or mechanical devices are recommended. Sampling devices that collect undisturbed samples include split-spoon samplers, ring samplers, continuous samplers, zero-contamination samplers, and Shelby tubes. These sampling devices can be used to collect surface soil samples or they can be used in conjunction with hollow-stem augers to collect subsurface samples. The soil sampling devices discussed above are summarized in Table 9. Devices where the soil samples can be easily and quickly removed and containerized with the least amount of disturbance and exposure to the atmosphere are highly recommended. U.S. EPA (1986a) gives a more detailed discussion on the proper use of drill rigs and sampling devices.

Liners are available for many of the devices listed in Table 9. Liners make soil removal from the coring device much easier and quicker. Liners reduce cross contamination between samples and the need for decontamination of the sampling device. The liner can run the entire length of the core or can be precut into sections of desired length.

When sampling for VOCs, it is critical to avoid interactions between the sample and the liner and between the sample and the sampler. Such interactions may include either adsorption of VOCs from the sample or release of VOCs to the sample. Gillman and O'Hannesin (1990) studied the sorption of six monoaromatic hydrocarbons in ground water samples by seven materials. The hydrocarbons included benzene, toluene, ethylbenzene, and o-, m-, and p-xylene. The materials examined were stainless steel, rigid PVC, flexible PVC, PTFE Teflon, polyvinylidene fluoride, fiberglass, and polyethylene. Stainless steel showed no significant sorption during an 8-week period. All polymer materials sorbed all compounds to some extent. The order of sorption was as follows: rigid PVC < fiberglass < polyvinylidene fluoride < PTFE < polyethylene < flexible PVC. Stainless steel or brass liners should be used since they exhibit the least adsorption of VOCs. Other materials such as PVC or acetate may be used, provided that contact time between the soil and the liner material is kept to a minimum. Stainless steel and brass liners have been sealed with plastic caps or paraffin before shipment to the laboratory for sectioning and analysis. VOC loss can result from permeation through the plastic or paraffin and volatilization through leaks in the seal. Acetate liners are available, but samples should not be held in these liners for any extended period, due to adsorption onto and permeation through the material. Alternatively, the soil can be extruded from the liner, and a portion can be placed into a wide-mouth glass jar. Smaller aliquots can be taken from the center of the precut liner using subcoring devices and the soil plug extruded into VOA vials.

TABLE 9. SOIL SAMPLERS FOR VOC ANALYSIS

Recommended	Not Recommended
Split spoon w/liners	Solid flight liners
Shelby tube (thin wall tubes)	Drilling mud auger
Hollow-stem augers	Air drilling auger
Veihmeyer or King tubes w/liners	Cable tool
	Hand augers
Piston samplers*	Barrel augers
Zero contamination samplers*	Scoop samplers
Probe-drive samplers	Excavating tools, e.g., shovels, backhoes

* May sustain VOC losses if not used with care

TRANSFER OF SOIL SAMPLES FROM DEVICE TO CONTAINER

The sample transfer step is perhaps the most critical and least understood step in the sampling and analysis procedure. The key point in sample transfer, whether in the field or in the laboratory, is to minimize disturbance and the amount of time the sample is exposed to the atmosphere. It is more important to transfer the sample rapidly to the container than to accurately weigh the aliquot which is transferred, or to spend considerable time reducing headspace. Therefore, a combination of a device for obtaining the appropriate mass of sample and placement of the aliquot into a container that can be directly connected to the analytical device in the laboratory is recommended. Several designs are available for obtaining a 5-g aliquot (or other size). Most subcoring devices consist of a plunger/barrel design with an open end. The device shown in Figure 3 was constructed by Associated Design & Manufacturing Company (Alexandria, VA). Other designs include syringes with the tips removed, and cork borers (Table 8). The device is inserted into the sample and an aliquot is withdrawn. The aliquot, which is of a known volume and approximate weight, can then be extruded into a tared 40-mL VOA vial. Routinely, the vial is then sealed with a Teflon-lined septum cap. Teflon, however, may be permeable to VOCs. Aluminum-lined caps are available to reduce losses due to permeation. At the laboratory, the vial must be opened and the contents of the vial must be transferred to a sparger tube. The transfer procedure will result in significant losses of VOCs from the headspace in the vial. The modified purge-and-trap cap shown in Figure 4 eliminates the loss of VOCs due to container opening and sample transfer. The soil is extruded from the subcorer into a tared 40-mL VOA vial and the modified cap is attached in the field. In the laboratory, the vial is attached directly to a purge-and-trap device without ever being opened to the ambient air.

Use of subcoring devices should produce analytical results of increased accuracy. In order to test this hypothesis, an experiment was conducted in which a bulk soil sample was spiked with 800 μg/kg of different VOCs (Maskarinec, 1990). Three aliquots were withdrawn by scooping, and three aliquots were withdrawn by using the sub-corer approach. The results are presented in Table 10. Although neither method produced quantitative recovery, the subcorer approach produced results that were generally

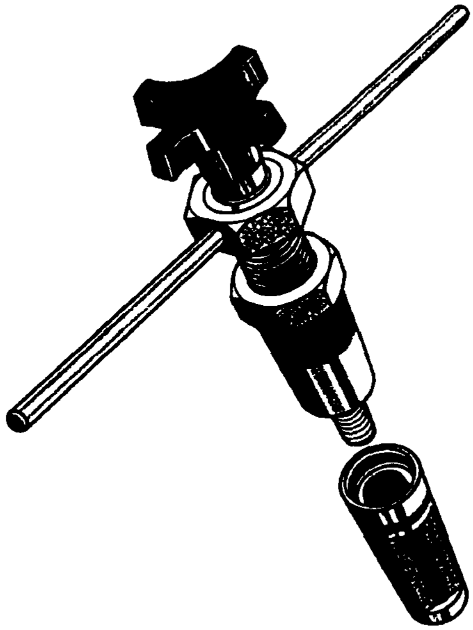

Figure 3. Small-diameter hand-held subcoring device made by Associated Design & Manufacturing Company (Alexandria, VA).

TABLE 10. LABORATORY COMPARISON OF STANDARD METHOD AND SUBCORER METHOD

Compound	Standard Method[a]	Subcorer Method[b]	Standard Method % of Recovery of Spike	Subcorer % of Recovery of Spike
Chloromethane	50	1225	6	153
Bromomethane	31	536	4	67
Chloroethane	78	946	10	118
1,1-Dichloroethene	82	655	10	82
1,1-Dichloroethane	171	739	21	92
Chloroform	158	534	20	67
Carbon tetrachloride	125	658	16	82
1,2-Dichloropropane	147	766	18	96
Trichloroethene	120	512	15	64
Benzene	170	636	21	80
1,1,2-Trichloroethane	78	477	10	60
Bromoform	30	170	4	21
1,1,2,2-Trichloroethane	46	271	6	34
Toluene	129	656	16	82
Chlorobenzene	57	298	7	37
Ethylbenzene	68	332	8	42
Styrene	30	191	4	24

[a] µg/kg (n=3)
[b] µg/kg (n=3)
Note: Standard method of sample transfer consists of scooping and subcorer method uses device shown in Figure 3. Soil samples were spiked with 800 µg/kg of each VOC.

five times higher than the standard approach, whereby the contents of a 125-mL wide-mouth jar are poured into an aluminum tray and homogenized with a stainless steel spatula. A 5-g sample is then placed in the sparger tube (SW-846, Method 8240). Several compounds presented problems with both approaches: styrene polymerizes, bromoform purges poorly, and 1,1,2,2-tetrachloroethane degrades quickly.

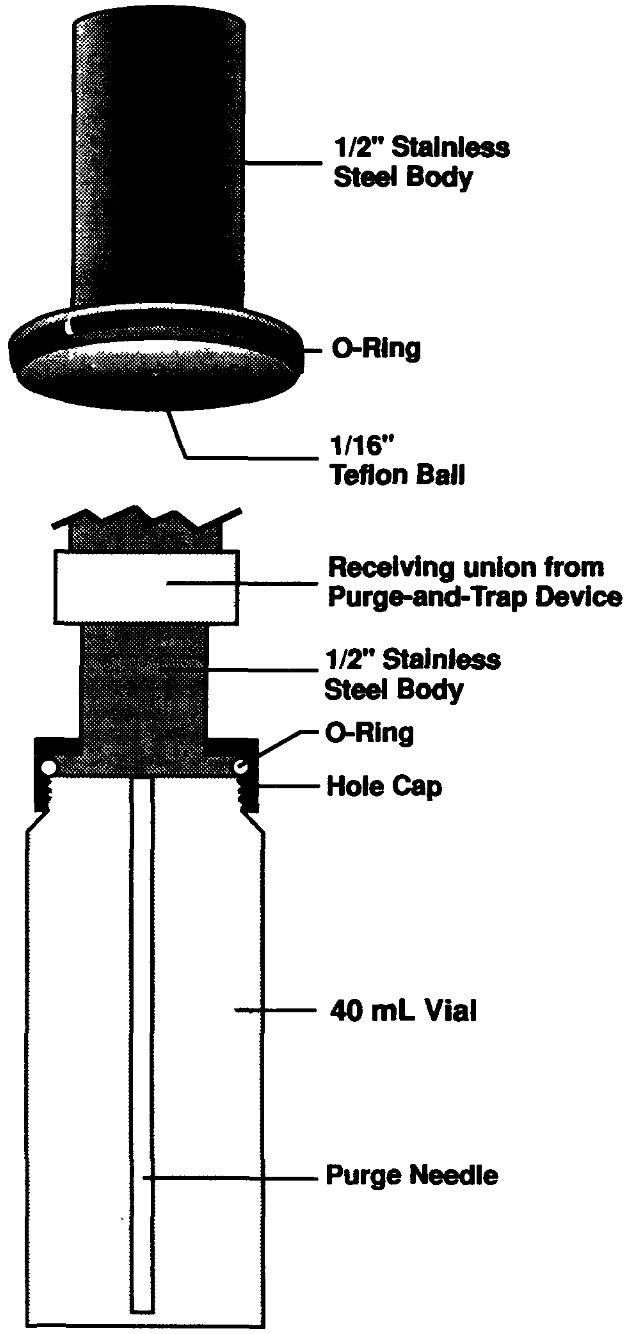

Figure 4. Modified purge-and-trap 40-mL VOA vial cap for containerizing samples in the field. Vial is attached directly to a purge-and-trap system without exposure of sample to the atmosphere.

In another study (U.S. EPA, 1991a), a large quantity of well characterized soil was spiked with 33 VOCs and was homogenized. From the homogenized material, a 5-g aliquot of soil was placed in a 40-mL VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The remaining soil was placed in 125-mL wide-mouth jars. The samples were shipped via air carrier and were analyzed by GC/MS with heated purge and trap. The 40-mL VOA vials were connected directly to a Tekmar purge-and-trap unit without exposure to the atmosphere. The wide-mouth jars were processed as per SW-846 Method 8240 specifications (U.S. EPA, 1986b). Table 11 compares the results of the GC/MS analyses using the two pretreatment techniques. The modified method (40-mL VOA vial with a modified cap) yielded consistently higher VOC concentrations than the traditional Method 8240 procedure (U.S. EPA, 1986b).

The standard methods for VOC analysis, SW-846, Method 8240 and Test Method 624 (U.S. EPA, 1986b; U.S. EPA, 1982), call for the containerizing of soil samples in 40-mL VOA vials or 125-mL wide-mouth jars with minimal headspace. As previously described, wide-mouth jars may not be the most appropriate containers due to sample aliquoting requirements. Although wide-mouth jars may be equally as effective as 40-mL VOA vials in maintaining the VOC content of soil samples, the sample preparation procedure that is required with jar-held samples causes significant (>80%) loss of highly volatile VOCs (Siegrist and Jennsen, 1990). However, if samples are collected in such containers, it is important to ensure sample integrity, preferably by using amber glass jars (for photosensitive compounds) with solid phenolic resin caps and foam-backed Teflon liners. Aluminum-lined caps are not available for the wide-mouth jars. Soil should be wiped from the threads of the jar to ensure a tight seal.

The methanol-immersion procedure calls for the transfer of the sample into a glass jar containing a known volume of chromatographic-grade methanol (usually 100 mL) or in a 1:1 weight-to-volume ratio of soil to methanol. This has the effect of preserving the volatile components of the sample at the time the sample is placed in the container. Furthermore, surrogate compounds can be added at this time in order to identify possible changes in the sample during transport and storage. The addition of methanol to the sample raises the detection limits from 5 to 10 µg/kg to 100 to 500 µg/kg, because of the attendant dilution. However, the resulting data have been shown to be more representative of the original VOC content of the soil (Siegrist and Jennsen, 1990; Siegrist, 1990). In a comparison of transfer techniques, Siegrist and Jennsen (1990) demonstrated that minimum losses were obtained by using an undisturbed sample followed by immediate

TABLE 11. COMPARISON OF VOC CONCENTRATIONS IN SPIKED SOIL ANALYZED BY METHOD 8240 AND MODIFIED METHOD 8240

VOC	Concentration (µg/kg) Method 8240†	Modified Method 8240††	Difference	VOC	Concentration (µg/kg) Method 8240†	Modified Method 8240††	Difference
Bromomethane	9	44	35**	Dibromochloromethane	121	159	38
Vinyl chloride	3	32	29**	1,1,2-Trichloroethane	142	193	51
Chloroethane	6	36	30**	trans-1,3-Dichloropropene	154	203	49
Methylene chloride	69	100	31**	Bromoform	116	140	24
Carbon disulfide	32	82	50**	Tetrachloroethene	62	124	62**
1,1-Dichloroethene	12	35	23**	1,1,2,2-Tetrachloroethane	137	162	25
1,1-Dichloroethane	34	83	49**	Toluene	85	161	76*
1,2-Dichloroethene	36	66	30**	Chlorobenzene	91	132	41**
Chloroform	56	96	40**	Ethylbenzene	85	135	50**
1,1,1-Trichloroethane	26	80	54**	Styrene	86	114	28*
Carbon tetrachloride	18	61	43**	Total xylenes	57	85	28**
Vinyl acetate	18	26	8				
1,2-Dichloroethane	101	159	58**	KETONES			
cis-1,3-Dichloropropene	136	189	53*	Acetone	336	497	161*
Trichloroethene	48	87	39**	2-Butanone	290	365	75
Benzene	56	114	58*	2-Hexanone	200	215	15
Bromodichloromethane	111	166	55*	4-Methly-2-pentanone	264	288	24

† Method 8240 using 125-mL wide-mouth jar mixing subsampling in laboratory purge/trap analysis.
†† Method 8240 using 40-mL vial. 5-g sampled in the field, shipped to laboratory purge/trap analysis.
** Difference significantly greater than 0, with P-value <0.01.
* Difference significantly greater than 0, with P-value between 0.01 and 0.05.
Note: Spike concentration was 300 µg/kg.

immersion into methanol. The results for six VOCs are shown in Figure 5. At high VOC spike levels (mg/kg) the investigators found that headspace within the bottle caused a decrease in the concentration of VOCs in the sample. At lower spike levels, however, headspace did not seem to be a major contributor to VOC losses (Maskarinec, 1990). In another study (U.S. EPA, 1991a), it was found that a 5-g sample collected from a soil core and placed in a 40-mL VOA vial provided consistently higher

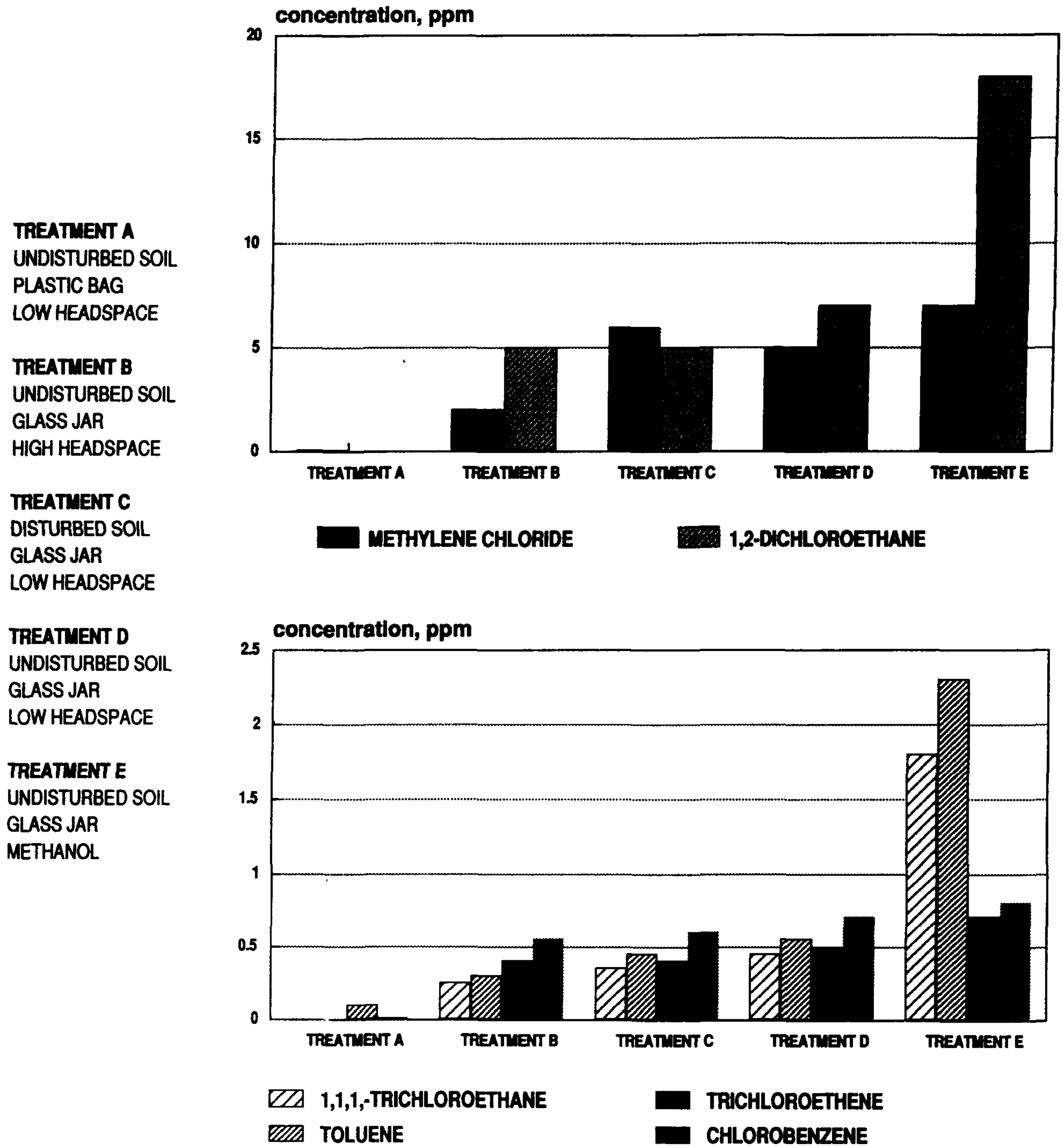

Figure 5. VOC recovery as a function of sample treatment.

VOC levels than a sample taken from the same core, placed in a 125-mL wide-mouth jar, and later poured out, homogenized, and a 5-g aliquot taken from the bulk material as per Method 8240 specifications.

SOIL SAMPLING SCENARIOS

The following recommendations for soil sampling and sample handling are presented for the three general sampling scenarios described earlier.

1. Open Test Pit or Trench

Samples are often collected from exposed test pits or trenches where remediation efforts are in progress. Sites may also be encountered where large-diameter coring devices cannot be employed. In such instances, crude sampling devices, such as trowels, spoons, shovels, spades, scoops, hand augers, or bucket augers must be used to excavate the soil.

The exposed face of an excavated test pit is scraped to uncover fresh material. Samples are collected from the scraped face by using a small-diameter, hand-held corer (Figure 3). If the nominal 5-g sample is to be collected, the appropriate volume (3 to 4 mL) is extruded into a tared 40-mL VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The vial is chilled to 0° to 4°C and sent to the laboratory where the entire contents of the vial are purged without opening the vial (U.S. EPA 1991b). Though this method minimizes losses of VOCs, the small sample size may exhibit greater short-range spatial variability than larger samples.

Alternatively, a small-diameter, hand-held soil corer (Figure 3) can be used to collect a larger volume of soil. The soil is extruded to fill a 40-mL VOA vial with a Teflon-lined septum cap (minimal headspace), chilled, and sent to the laboratory. The major weakness with this method is that VOCs are lost in the laboratory during sample homogenization, preparation of aliquots from a subsample, and the transfer to the extraction or sparging device.

If large coarse fragments or highly compacted soils are encountered, the use of a hand-held corer may not be possible. In this case crude sampling devices are used to rapidly collect and fill (minimal headspace) a 125- or 250-mL wide-mouth glass jar. The threads are wiped clean and the jar is sealed with a foam-backed Teflon-lined cap. The jar is chilled immediately to 0° to 4°C for shipment to the laboratory. Losses of VOCs are considerably greater with this method due to disruption of the matrix and losses in the laboratory during sample preparation. Methanol immersion may be more suitable for these matrices.

2. Surface Soils (< 5 ft deep)

The preferred soil sampling procedures reduce VOC losses by minimizing sample disturbance during collection and transfer to a container. The collection of soil cores with direct extrusion into a container accomplishes this goal. A larger-diameter coring device (e.g., split-spoon sampler, Shelby tube, zero-contamination sampler) is used to collect an intact sample from the surface soil or from an augered hole. Many of these samplers can be used with liners, an insert that greatly reduces the time required to remove the soil and obtain a subsample. For subsamples collected from split spoons or extruded large-diameter cores, the section to be subsampled is scraped and laterally subcored, or the extruded soil is cut or broken to expose fresh material at the depth or zone of interest, then longitudinally subcored. For large-diameter cores that are collected in precut liners, the liner sections are separated with a stainless steel spatula, and a small-diameter hand-held corer is used to collect a subsample from the center of the liner section. The uppermost portion of the core should not be sampled, because it is more likely to be cross contaminated. The small diameter corer (Figure 3) is pushed into the soil, the outside of the corer is wiped clean, and the required core volume (typically about 3 to 4 mL or 5 g) is extruded directly into a tared 40-mL glass VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The vial threads and lip must be free of soil to ensure an airtight seal.

3. Subsurface soils (> 5 ft deep)

The same sampling principles apply for the collection of deeper soil samples. Collection of soil cores with direct extrusion into a container greatly reduces the loss of VOCs. Tube-type samplers such as split-spoon, Shelby tubes, and zero-contamination samplers are used inside a hollow-stem auger to obtain an intact sample from greater depths. The coring device is retrieved and a subsample is obtained in a similar manner as that described for surface soils.

METHANOL IMMERSION PROCEDURE

Soil collected by protocols outlined above can be placed in a tared wide-mouth glass jar containing pesticide-grade methanol (1:1 weight-to-volume ratio of soil to methanol). The immersion of relatively large soil samples into methanol has the advantage of extracting a much larger sample that is probably less prone to short-range spatial variability. This is of particular advantage with coarse-grained soils, materials from which it is hard to obtain a 1-g to 5-g subsample for analysis.

Multiple small-diameter corers can be immersed in a single methanol-filled jar to produce a composite sample. Compositing becomes practical because VOCs are soluble in methanol, thus reducing losses. Appropriately collected composite samples can produce more representative data than a comparable number of individual samples. Short-range spatial variability is greatly reduced. Another advantage is the ability to reanalyze samples. The main disadvantages of using methanol include the requirements for handling and shipping the methanol and the detection limit that is raised by a factor of about 10 to 20. For the methanol-immersion procedure, jars filled with methanol and shipped to the laboratory are classified as a hazardous material, flammable liquid and must be labelled as per Department of Transportation specifications (49 CFR, 1982). If these disadvantages are unacceptable, then the modified purge-and-trap procedure may be applicable.

FIELD STORAGE

Material containing VOCs should be kept away from the sample and the sample container. Hand lotion, labeling tape, adhesives, and ink from waterproof pens contain VOCs that are often analytes of interest in the sample. Samples and storage containers should be kept away from vehicle and generator exhaust and other sources of VOCs. Any source of VOCs may cause contamination that may compromise the resulting data.

Once samples are removed from the sampling device and placed in the appropriate storage container, the containers should be placed in the dark at reduced temperatures (0° to 4°C). Excessively cold temperatures (<-10°C) should be avoided; studies have shown greater losses of analytes due to reduced pressures in the container, sublimation of water, and concomitant release of water-soluble VOCs into the headspace. Upon opening the container, the vacuum is quickly replaced with ambient air, thus purging out VOCs from the headspace (Maskarinec et al., 1988). Extremely cold temperatures can also loosen the seal on the container cap. Caps should be retightened after 15 minutes at reduced temperatures. Samples should be kept in ice chests while in route to the shipment facility or laboratory. At temperatures above freezing, bacterial action can have a significant impact on the observed soil VOC concentration. Numerous preservation techniques are being evaluated at the University of Nevada Environmental Research Center in Las Vegas and at Oak Ridge National Laboratory.

SHIPPING

Given the short holding times required for VOC analysis under Method 8240 (10 days from sample collection to analysis), samples are usually shipped via air carrier to the analytical laboratory. Samples should be well packed and padded to prevent breakage. Temperatures in cargo holds can increase to more than 50°C during transit, therefore, the need for adequate cold storage is critical. Styrofoam coolers are commercially available to accommodate 40-mL and 125-mL glass containers. Sufficient quantities of Blue Ice™ or Freeze-Gel™ packs should be placed in the container to ensure that samples are cooled for the duration of the shipment. A maximum-minimum thermometer (non-mercury) should be shipped with the samples. If sample containers are not adequately sealed, VOC losses can occur. These losses may be exacerbated by the reduced atmospheric pressures encountered in the cargo holds of air carriers. Figure 6 illustrates the changes in temperature and pressure in the cargo hold of various air carrier's aircraft. Three major air carriers have been monitored and have shown similar fluctuations in temperature and pressure (Lewis and Parolini, 1991). Lewis et al. (1990) noted decreases in VOC concentrations in soil samples that were shipped compared to samples that were analyzed in the field. If the container is of questionable or unknown integrity, it should either be evaluated prior to use or a previously characterized container should be used.

As discussed previously, samples that are immersed in methanol have special shipping requirements. These samples must be shipped as "Flammable Liquids" under Department of Transportation (DOT) requirements. A secondary container is required for shipment of any item classified as a flammable liquid.

PRESERVATION

Improvements in operational factors such as sampling device efficiency, sample transfer, containerizing, shipping, storage, laboratory sample preparation, and analysis will reduce VOC losses from soils. Two principal matrix-specific factors that can contribute to the loss of VOC in soils are biodegradation and volatilization. An effective preservation technique should act on these matrix-specific factors to reduce losses of VOCs.

The required preservation technique for soil samples is storage at 0° to 4°C in the dark. This technique retards biodegradation

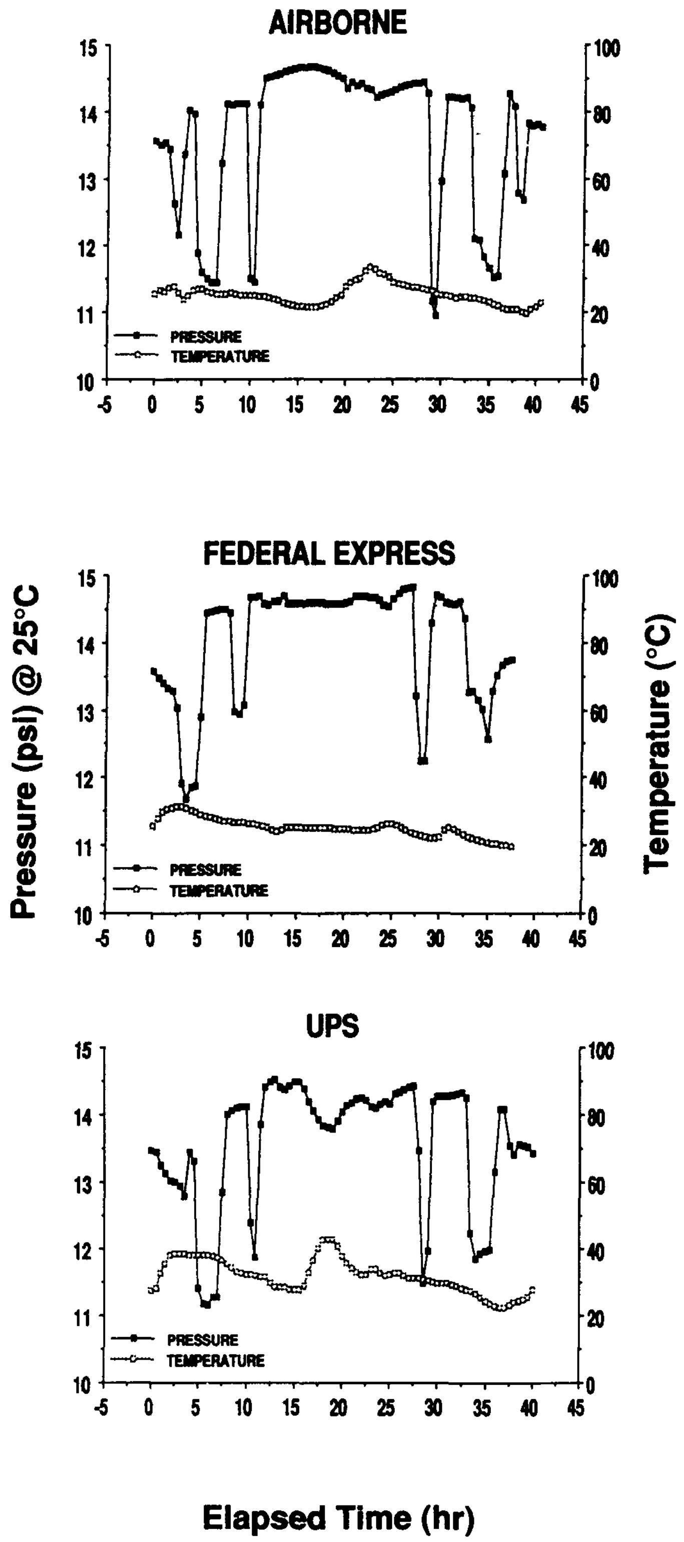

Figure 6. Temperature and pressure fluctuations recorded in the cargo hold of various air carriers. Recording device was shipped from Las Vegas, NV, to Pearl River, NY, and returned.

processes mediated by soil microorganisms. Some microorganisms, however, such as fungi, are biologically active even at 4°C. Wolf et al. (1989) investigated several methods (i.e., chemical and irradiation) for sterilizing soil and concluded that mercuric chloride is one of the most effective preservatives that causes minimal changes to the chemical and physical properties of the soil. Stuart et al. (1990) utilized mercuric chloride as an antimicrobial preservative to stabilize ground-water samples contaminated with gasoline. Other researchers (U.S. EPA 1991a) have used mercuric chloride to retard biodegradation of VOCs in soil samples. The soils were spiked with 150 µg/kg of Target Compound List (TCL) VOCs and were preserved with 2.5 mg of mercuric chloride per 5 g of soil. The results indicated that the amount of mercuric chloride needed to reduce biodegradation was directly related to the soil's organic carbon content. In addition, the levels of mercuric chloride added to samples did not interfere with sample handling or analysis. Currently, research is underway to quantitate the required mercuric chloride concentration as a function of soil organic content.

The loss of VOCs through volatilization is reduced by optimizing sample handling procedures. When samples require laboratory pretreatment, severe losses of VOCs (up to 100%) have been observed. In order to minimize volatilization losses, several preservatives have been examined (U.S. EPA 1991a), including solid adsorbents, anhydrous salts, and water/methanol extraction mixtures. The most efficient preservatives for reducing volatilization of VOCs from soils have been two solid adsorbents, Molecular Sieve - 5A™ (aluminum silicate desiccant) and Florasil™ (magnesium silicate desiccant). The addition of 0.2 mg per 5 g of soil greatly increased the recovery of VOCs from spiked samples. The mechanism is believed to involve the displacement of water from adsorption sites on the soil particle and binding of VOCs to these freed sites. Currently, research is in progress with soils obtained from actual contaminated sites.

LABORATORY PROCEDURES

Sample Storage

Most regulatory procedures specify storage of samples for VOA at 4°C in the dark. Sample coolers should be opened under chain-of-custody conditions, and the temperature inside the cooler should be verified and noted. Samples should be transferred to controlled-temperature (4°C) refrigerators until analysis. In many cases, insufficient cooling is provided during transport. In these cases, data quality may be compromised.

Sample Preparation

The two most commonly used methods that satisfy regulatory requirements for the analysis of soil samples for VOCs are direct purge and trap and methanol extraction. Each procedure has benefits and limitations with respect to sample preparation prior to VOC analysis of soils.

The modified purge-and-trap procedure has the following characteristics:

- Homogenization of contents of wide-mouth jar will cause significant VOC losses. The collection of a 5-g aliquot in the field and placement into a tared vial sealed with a modified purge-and-trap cap is recommended.
- Surrogate addition should be made to the soil in the field, if possible.
- May be more susceptible to short-range spatial variability.
- Samples should be brought to ambient temperature before purging.
- May be more suitable for low-level samples.

The methanol-immersion procedure has the following characteristics:

- The key is to minimize the time samples are exposed to the atmosphere prior to immersion into methanol.
- Minimum detection limits can be raised by a factor of 10 to 20.
- The best option for sample archival because VOCs are highly soluble in methanol.
- Large-mass samples can be extracted in the field in a 1:1 ratio and the methanol extract shipped to the laboratory for analysis.
- Can collect composite samples.

The analytical methods that can be used for the analysis of soils for VOCs are summarized in Table 12. An analytical method should be selected that is compatible with the recommended sample collection and containerizing procedure discussed earlier.

CONCLUSIONS AND RECOMMENDATIONS

Current research on sampling soils for VOC analyses answers many of the questions asked by RPMs and OSCs who conduct site characterization and restoration.

1. There is no specific method or process that can be recommended for sampling soils for VOA. A wide variety of sampling devices are currently used for collecting soil samples for VOA. Sampling device selection is site-specific, and no single device can be recommended for use at all sites. Several different samplers, which cover a broad range of sampling conditions and circumstances, are recommended for obtaining representative samples for VOC analysis (Table 7). Procedures may vary for different VOCs. Experiments have shown that a procedure that collects an undisturbed, intact sample with a device that allows direct transfer to a sample container (e.g., split-spoon, Shelby tube, or zero-contamination sampler) is superior to a more disruptive procedure that uses a crude bulk sampler (e.g., shovel, trowel, scoop, or spade) for maintaining the integrity of VOCs in a soil sample. Large-diameter tube-type sampling devices are recommended for collection of near-surface samples. The same types of devices can be used in conjunction with hollow-stem augers for collecting subsurface samples.
2. Transfer of the sample from the sampling device to the container is a critical step in the process. Losses of as much as 80% have been observed during this step. The faster the soil can be removed from the sampling device and

TABLE 12. METHODS FOR VOC ANALYSIS OF SOIL

Method Extraction/analysis	Sample Size (g)	Sample Preparation Procedure	Sensitivity (µg/kg)	Data Quality Objective	Program	Comments
5030 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5	Purge and trap	5-10	Litigation	RCRA[a]	Sample transfer to purge and trap is critical.
5380 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5-100	Methanol extraction	500-1000	Litigation	RCRA	Sensitivity loss but sample transfer facilitated.
5031 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5	Field purge	5-10	Semi-quantitative	RCRA	Sample can only be analyzed once, transfer and shipping facilitated.
3810 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	10	Heat to 90°C in water bath and analyze headspace	1000	Screening for purgeable organics	RCRA	Can be performed in the field.
3820	10	Hexadecane extraction followed by GC/FID	500-1000	Screening prior to GC or GC/MS analysis	RCRA	FID responses vary with type of VOC.
624	5	Purge and trap	5-10	Litigation	CLP[b]	Similar to method 5030/8240 in RCRA SW-846.

[a] U.S. EPA, 1986b
[b] U.S. EPA, 1982

transferred into an airtight sample container, the smaller the VOC loss. Liners make the removal and subsampling of soil from the collection device more efficient.

3. The best method for transferring a sample from a large-diameter coring device (or exposed test pit) into a sample container is by collecting the appropriate size aliquot (for laboratory analysis) with a small-diameter, hand-held corer and extruding the subsample into a 40-mL VOA vial, then sealing the vial with a modified purge-and-trap cap. Alternatively, contents of the large-diameter coring device can be sectioned and immersed in methanol.

4. Small-diameter, hand-held corers can be used for collecting samples from a freshly exposed face of a trench or test pit, or for obtaining a subsample from a large-diameter coring device. The use of a small-diameter, hand-held corer is recommended for obtaining subsamples from liner-held soil. Collection of a sample of the appropriate size for a particular analytical procedure is optimal. The required size of aliquot can be extruded into a 40-mL VOA vial and sealed with a modified purge-and-trap cap. The possibility exists of compositing several small-diameter core samples by immersing them in a single jar containing methanol.

5. Sample containers vary in terms of air-tightness. Data are available to indicate that there is a decrease in pressure and an increase in temperature in the cargo holds of certain air carriers. This is the worst possible set of conditions for maintaining VOCs in containerized soil samples. Intact seals on storage containers and adequate cooling is thus critical for maintaining VOCs in soil samples. Shipping and holding-time studies have shown that vials and jars may be equally suited for containing VOCs in soil samples, the laboratory pretreatment step needed to obtain an aliquot from a jar-held sample causes significant losses of VOCs. Commercially available shipping packages with built-in cooling materials (e.g., Freeze Gel Packs® or Blue Ice®) are available. Whenever possible, an integrated sampling approach should be employed to obtain the most representative samples possible. Soil-gas surveying coupled with on-site soil sampling and analyses followed by the Resource Conservation and Recovery Act (RCRA) or CLP laboratory analyses may provide valuable information on the partitioning of VOCs at a site.

6. The current preservation technique for soil samples is storage at 4°C in the dark. Biological activity may continue at this temperature. The addition of mercuric chloride to the soil may reduce biodegradation of VOCs. The amount of mercuric chloride to be added, however, is a function of the organic carbon content in the soil. The most promising preservatives for reducing losses of VOCs through volatilization are solid adsorbents such as Molecular Sieve - 5A™ and Florasil™.